AD-A141 495

SYNTHESIS OF ENERGETIC MATERIALS
ANNUAL PROGRESS REPORT FOR THE
OFFICE OF NAVAL RESEARCH

WORK REQUESTS NO001483WR30134 AND
NO01484WR24121
PROJECT RR024-02-01/02-OD

By H. G. Adolph
    M. Chaykovsky
    J. M. Goldwasser
    W. M. Koppes

March 1984

Research and Technology Department

NAVAL SURFACE WEAPONS CENTER
Dahlgren, VA 22448 - Silver Spring MD 20910

DTIC FILE COPY

DTIC
ELECTE
MAY 2 4 1984
S D
A

84   05 23 068

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A141 495	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Synthesis of Energetic Materials		5. TYPE OF REPORT & PERIOD COVERED Annual Progress Report 1983
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) H. G. Adolph, M. Chaykovsky, J. M. Goldwasser, and W. M. Koppes		8. CONTRACT OR GRANT NUMBER(s) Work Request N0001483WR30134 N0001484WR24121
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center (Code R11) White Oak, Silver Spring, Maryland 20910		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61153N;RR024-02
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Code 432 Arlington, Virginia 22217		12. REPORT DATE 31 March 1984
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

Reproduction in whole or in part is permitted for any purpose of
the United States Government.

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Nitrodiols; Polyformals; Nitropolymers; Nitramines; Diazocines;
Azabicyclononanes; Azaadamantanes

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

An improved, novel method for the synthesis of the energetic polymer
precursors, 3,3-dinitropropanol-1, and 3,3,5,5,7-pentanitro-5-azanonane-
diol-1,9, 1, is described. The preparation of polyformals of 1 has been
investigated, and selected polymers of this type have been characterized.
The cross-linking reaction with a triisocyanate for a typical polyformal of
1 was demonstrated. The synthesis of 3,3,5-trinitro-5-azaheptane-diol-1,7
was accomplished, and the formation of a polyformal on reaction with

CH_2O/BF_3 etherate was observed. 2,2,3,3,4,4-hexafluoropentanediol-1,5 gave higher molecular weight polyformals (up to M.W. 10,000) than previously reported on reaction with CH_2O/conc. H_2SO_4.

In efforts to synthesize polycyclic nitramines, potential routes to bicyclo-HMX from 2,4,6,8-tetraacetyl-2,4,6,8-tetrazabicyclo(3.3.0)octane were examined, but the synthesis of the target compound was not achieved. Several ring di- and tetrasubstituted derivatives of piperazine were synthesized, and condensation reactions with appropriate substrates toward bi- and polycyclic ring systems were investigated. A study of methods for the synthesis of diaza- and tetrazacyclooctadienes via elimination reactions with suitably substituted saturated precursors has been initiated.

CONTENTS

ILLUSTRATIONS
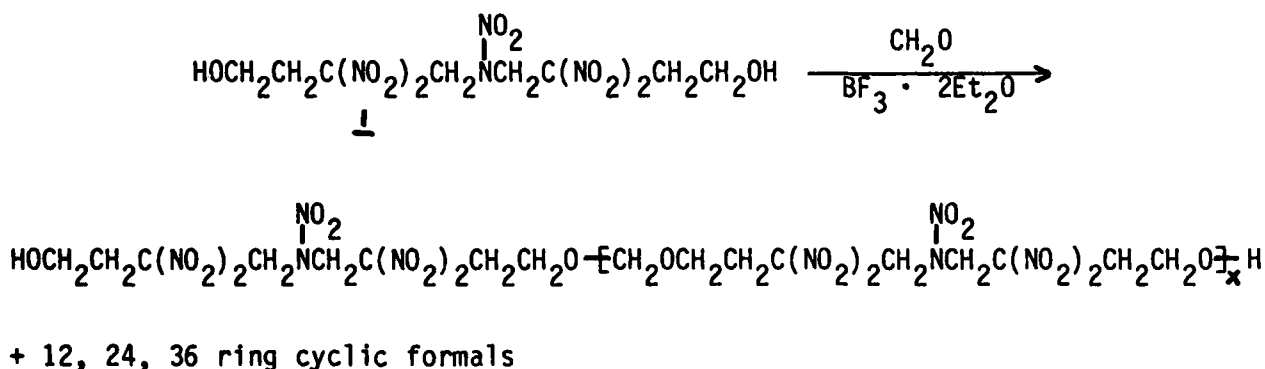
TABLES

SYNTHESIS OF ENERGETIC MATERIALS

INTRODUCTION

The work described in this report was carried out during 1983 under the sponsorship of the Office of Naval Research, Code 432 (Dr. R. S. Miller). The effort consisted of two separate tasks which will be discussed in turn: (1) synthesis of energetic monomers and polymers, and (2) synthesis of polycyclic and adamantoid nitramines. Both tasks were continuations of previous work, and pre-1983 results were reported in ref. 1. The principal objectives of the work are the synthesis of energetic (nitro) polymers with improved energy and physical properies, specifically polyformals derived from nitro substituted diols, and the synthesis of nitramines with high crystal density and energy-density greater than HMX.

ENERGETIC POLYMER AND MONOMER SYNTHESIS

In continuation of the previous work[1] under this task, the formation of hydroxy-terminated polyformals from selected nitrodiols was investigated further.
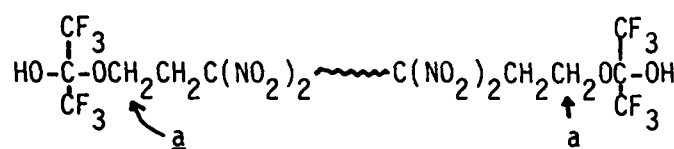
It had been shown in last year's work that 3,3,5,7,7-pentanitro-5-azanonanediol (1) on reaction with CH_2O/BF_3 etherate formed a mixture of linear and some cyclic polyformals, the former being hydroxy-terminatd and thus cross-linkable with di/triisocyanates.

$$HOCH_2CH_2C(NO_2)_2CH_2 \overset{NO_2}{\underset{|}{N}}CH_2C(NO_2)_2CH_2CH_2OH \quad \xrightarrow[BF_3 \cdot 2Et_2O]{CH_2O}$$

$$\underset{\mathbf{1}}{}$$

$$HOCH_2CH_2C(NO_2)_2CH_2 \overset{NO_2}{\underset{|}{N}}CH_2C(NO_2)_2CH_2CH_2O \{CH_2OCH_2CH_2C(NO_2)_2CH_2 \overset{NO_2}{\underset{|}{N}}CH_2C(NO_2)_2CH_2CH_2O\}_x H$$

+ 12, 24, 36 ring cyclic formals

In view of its high energy content and good solubility in energetic plasticizers, this polyformal appeared of interest as a cast-curable binder component, and additional effort was expended on its synthesis and characterization as well as on the synthesis of the diol 1 and its precursors. Also investigated was the possibility of obtaining other diols and polyformals from the precursor to 1, 2,2-dinitro-1,4-butanediol-4-acetate.

To optimize the preparation of the polyformal of 1, the effects of varying the reaction solvent, monomer concentration, diol/formaldehyde ratio, and condensing agent type and amount were studied. It was found that sulfolane was the preferred solvent, and that high monomer concentration and diol:formaldehyde ratios of about 10:9 gave the best results in terms of

completeness of reaction, cyclic formal content, and polymer molecular
weight. A typical run consists of reacting a solution of diol and trioxane in
sulfolane (1g diol/ml sulfolane) with BF_3 etherate at ambient temperature for
16-20 hours. The reaction is carried out under nitrogen, but is not highly
sensitive to the presence of moisture. Precipitation into methanol/water and
trituration of the polymer with dichloromethane/hexane is used to remove
sulfolane and reduce cyclic formal as well as low oligomer and monomer
content. Polymer yields at this point ranged from 80-85%. It was shown that
the mixture of unreacted monomer and low molecular weight formal is readily
hydrolized (by heating with aq. MeOH/conc. HCl) to 1 which can be reused for
polymer preparation. The purified polymer was characterized by GPC under
standard conditions. The OH content was determined by NMR analysis of its
hexafluoroacetone adduct and comparison of the terminal methylene signal (a)
area with that of an internal standard. Table 1 summarizes conditions and

$$HO-\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-OCH_2CH_2C(NO_2)_2 \text{~~~~} C(NO_2)_2CH_2CH_2O\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-OH$$

polymer data for a number of the runs made in this study. The weight fraction
of polymers was calculated with the assumption that the non-functional
component in the sample is the trimeric cyclic formal

$$[CH_2OCH_2CH_2C(NO_2)_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2CH_2O]_3$$
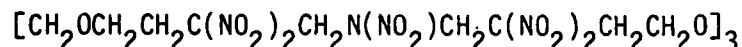
as indicated by the GPC, and that the linear component is hydroxy-terminated
and difunctional. The corrected molecular weights and poly-dispersity refer
to this linear component. The GPCs of runs 45/5 and 49/4 are shown in
Figures 1 and 2, respectively.

Run #49/4 was scaled up to the 10 g level without difficulty, except that
a larger amount of trioxane was inadvertently used. Not unexpectedly, this
resulted in a polymer of higher molecular weight and greater cyclic formal
content ($\approx$20%). This material was still soluble in FEFO (polymer:plasticizer
ratio 1:2), and the solution was shown to be cross-linkable with PAPI-135
using dibutyltin dilaurate as catalyst. The gumstock had good strength and
elongation. Unlike an earlier gumstock, however, it contained some bubbles.
These are believed to be caused by the excess formaldehyde not removed
completely during the purification of the polymer. This run will be repeated
using appropriate amounts of formaldehyde and a modified washing procedure
(addition of H_2O_2) to destroy unreacted formaldehyde.

Attempts were made also to improve and simplify the preparation of the
monomer 1 whose synthesis was described in an earlier report.[2] Using as
previously 2,2-dinitro-1,4-butanediol-4-acetate 2 as intermediate, the Mannich
reaction of the 4-acetate to give the azanonanediol diacetate was improved to
a 92-95% yield; the nitration and hydrolysis give 95%+ yields, also. Thus,
this part of the synthesis of 1 is well in hand.

TABLE 1. PREPARATIONS OF POLYFORMAL OF <u>1</u> ON 1 G SCALE IN SULFOLANE

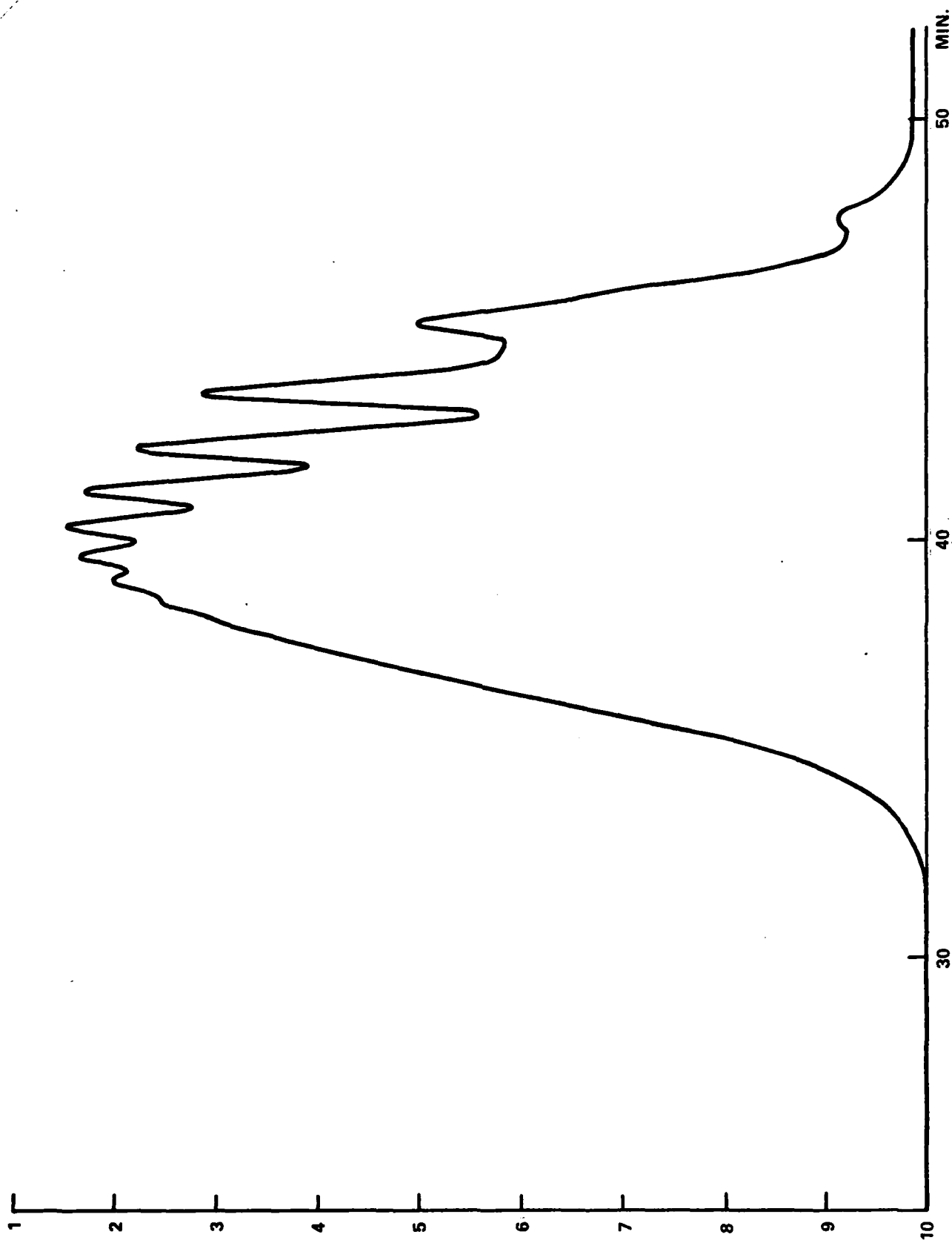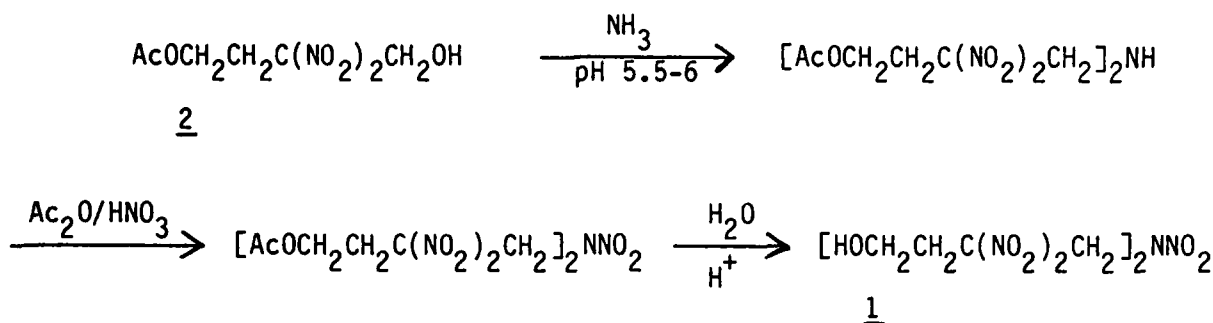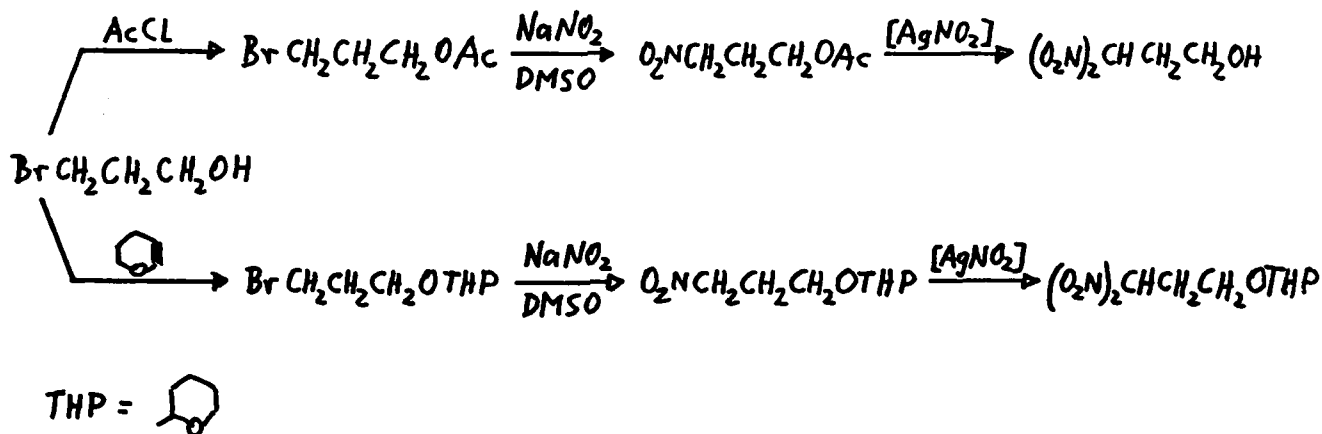| Run #5	ml Solvent	mg CH_2O	Molecular Weight (by GPC) M_n	Equivalent Weight (NMR)	Weight Fraction Polymer	Corrected Molecular Weight		D (M_w/M_n)
						M_w	M_n	
45/3	1.5	77.5	2045	1248	0.89	3519	2232	1.58
45/5	1.5	72.5	2040	1282	0.88	3686	2252	1.64
45/7	1.5	62.0	1318	--	--	--	--	--
49/1	1.5	66.6	1673	1146	0.81	2906	1850	1.57
49/3	1	66.6	1610	883	0.94	2595	1645	1.58
49/4	1	69.9	1720	963	0.93	2838	1790	1.58
49/5	1	72.5	1690	1034	0.87	2879	1800	1.60
49/6	1	75.0	1775	995	0.93	2993	1847	1.62

3
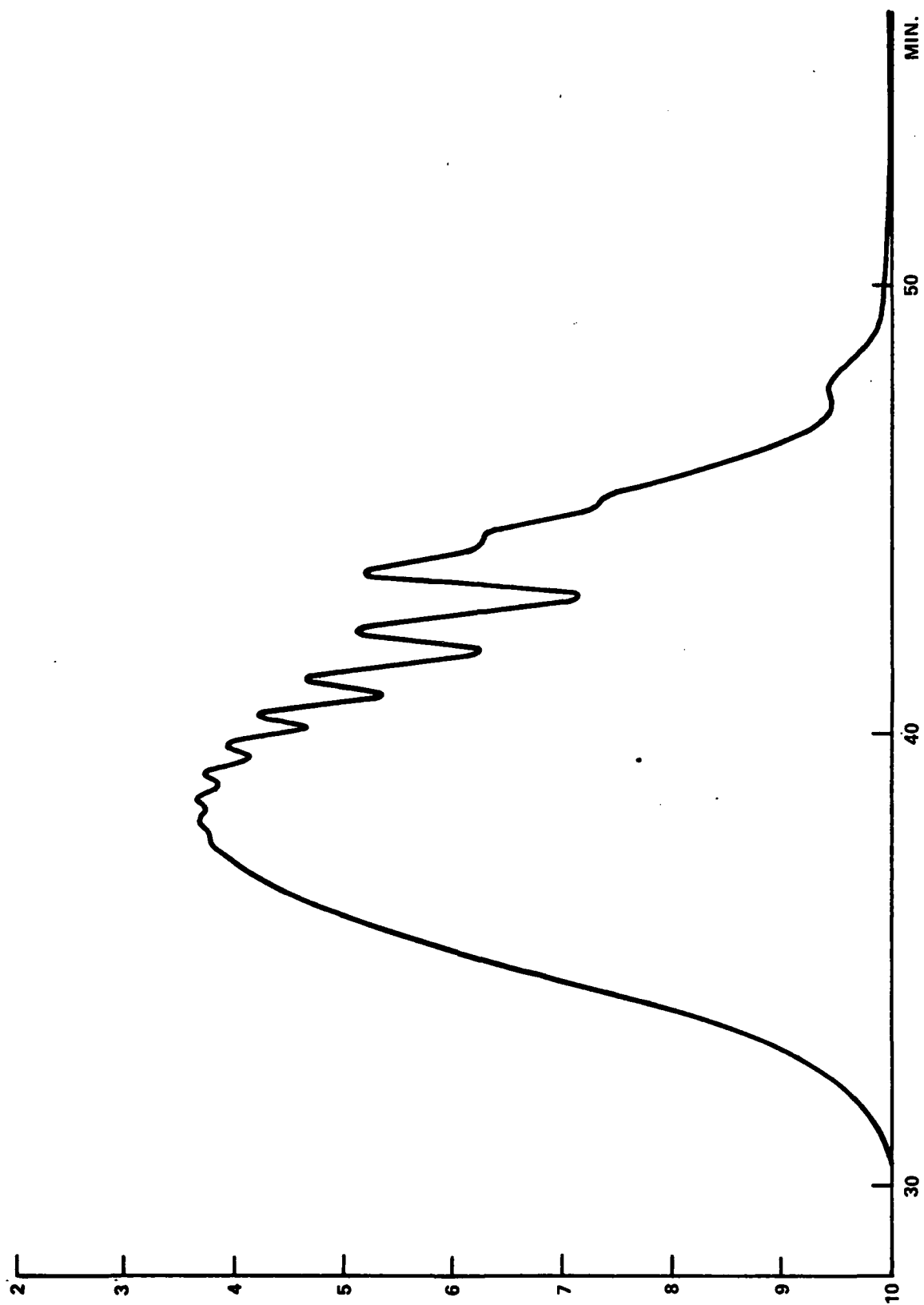
FIGURE 1. GP CHROMATOGRAM OF POLYFORMAL OF 1; RUN 45/5

4

FIGURE 2. GP CHROMATOGRAM OF POLYFORMAL OF 1; RUN 49/4

$$AcOCH_2CH_2C(NO_2)_2CH_2OH \xrightarrow[\text{pH 5.5-6}]{NH_3} [AcOCH_2CH_2C(NO_2)_2CH_2]_2NH$$

$$\underline{2}$$

$$\xrightarrow{Ac_2O/HNO_3} [AcOCH_2CH_2C(NO_2)_2CH_2]_2NNO_2 \xrightarrow[H^+]{H_2O} [HOCH_2CH_2C(NO_2)_2CH_2]_2NNO_2$$
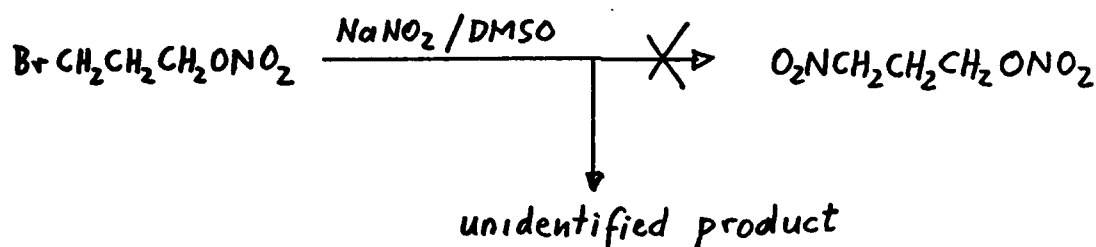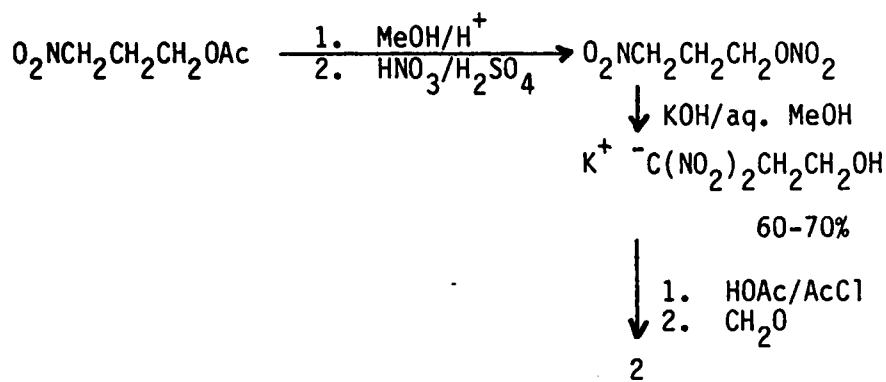
$$\underline{1}$$

Considerable effort was expended on working out a simpler synthesis for the mono-acetylated 2,2-dinitro-1,4-butanediol. The acetate and tetrahydropyranyl ether of commercially available 3-bromopropanol were converted to the corresponding 3-nitro compounds by a slight modification of the Kornblum synthesis. This was followed by oxidative nitration to 3,3-dinitro compounds. The yields in both steps are near 60% for the tetrahydropyranyl derivative, and further improvements are believed possible. The acetate, on the other hand, gave de-protected 3,3-dinitropropanol in low yield in the oxidative nitration.

$$BrCH_2CH_2CH_2OH$$

$$\xrightarrow{AcCl} BrCH_2CH_2CH_2OAc \xrightarrow[DMSO]{NaNO_2} O_2NCH_2CH_2CH_2OAc \xrightarrow{[AgNO_2]} (O_2N)_2CHCH_2CH_2OH$$

$$\xrightarrow{\text{(THP)}} BrCH_2CH_2CH_2OTHP \xrightarrow[DMSO]{NaNO_2} O_2NCH_2CH_2CH_2OTHP \xrightarrow{[AgNO_2]} (O_2N)_2CHCH_2CH_2OTHP$$

$$THP = \text{(cyclic ether)}$$

A method for the conversion of the tetrahydropyranyl ether to $\underline{2}$ has been worked out.

$$(O_2N)_2CHCH_2CH_2OTHP \xrightarrow[\substack{1.\ MeOH/HCl \\ 2.\ AcOH/AcCl \\ 3.\ CH_2O}]{} HOCH_2(O_2N)_2CCH_2CH_2OAc$$

$$75\%$$
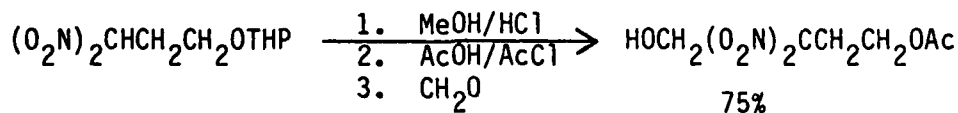
An alternative, probably more advantageous synthesis of $\underline{2}$ via 3,3-dinitropropanol as shown below eliminates the need for the oxidative nitration step. At present, the required 3-nitropropyl nitrate is prepared from the acetate in two steps, as the attempted direct synthesis from 3-bromopropyl nitrate gave a different, not yet identified product.

6

$$O_2NCH_2CH_2CH_2OAc \xrightarrow[\text{2. } HNO_3/H_2SO_4]{\text{1. } MeOH/H^+} O_2NCH_2CH_2CH_2ONO_2$$

$$\downarrow KOH/aq.\ MeOH$$

$$K^+\ {}^-C(NO_2)_2CH_2CH_2OH$$

$$60\text{-}70\%$$

$$\downarrow \begin{array}{l}\text{1. } HOAc/AcCl \\ \text{2. } CH_2O\end{array}$$
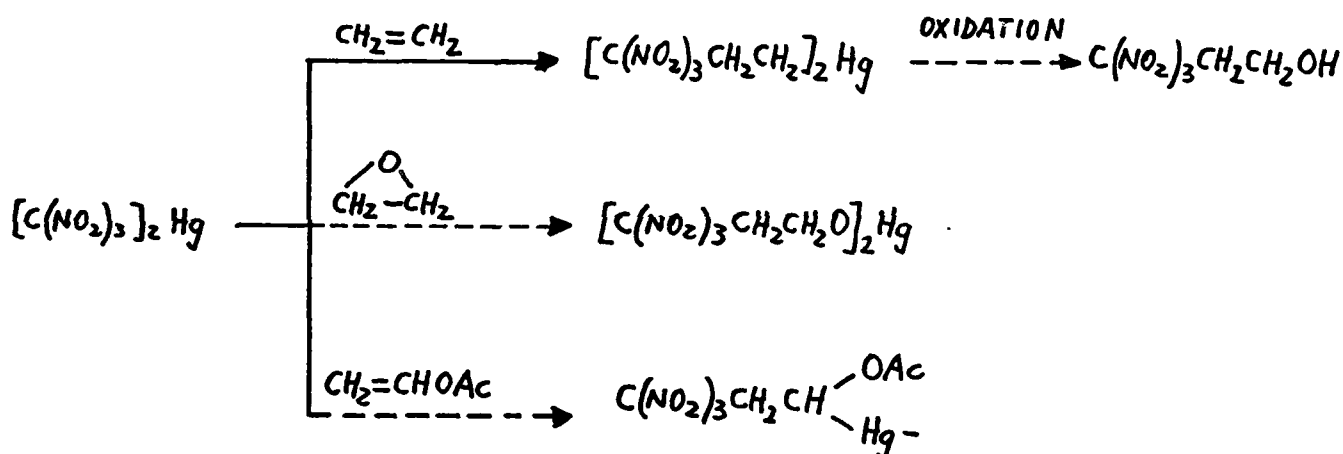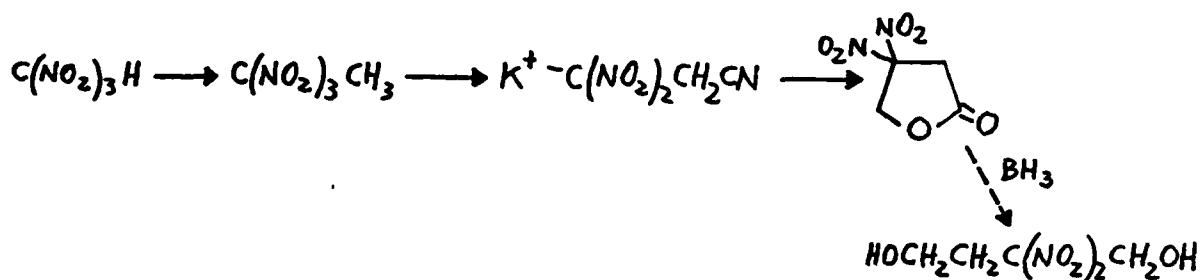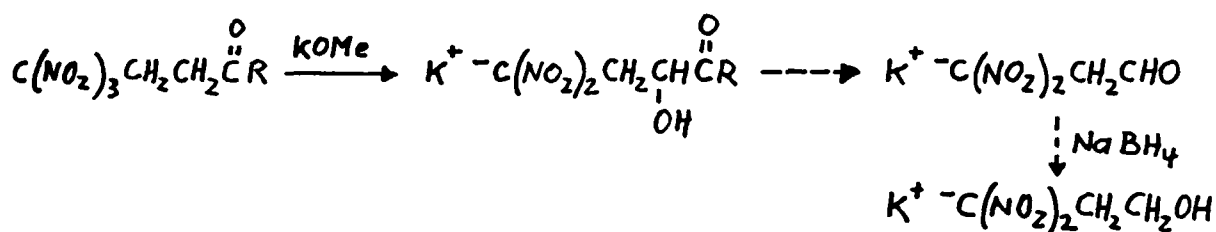
$$\underline{2}$$

$$BrCH_2CH_2CH_2ONO_2 \xrightarrow{NaNO_2/DMSO} \xcancel{} O_2NCH_2CH_2CH_2ONO_2$$
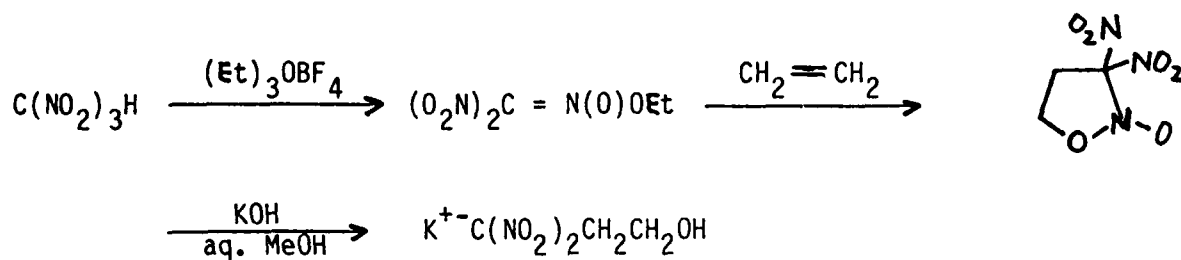
$$\downarrow$$

unidentified product

Several other routes to 2,2-dinitro-1,4-butanediol starting from nitroform have been or are being investigated. 4,4,4-trinitrobutyronitrile can reportedly be converted to 3,3-dinitropropionaldehyde,[3] but we were unable to repeat this reaction. However, 5,5,5-trinitro-2-pentanone and 4,4,4-trinitrobutyrates give dinitrohydroxycarbonyl compounds on treatment with base,[4] and these should be convertible to 3,3,-dinitropropionaldehyde and 3,3-dinitripropanol by known procedures. Another route from nitroform proceeds via trinitroethane, 3,3-dinitropropionitrile, and 3,3-dinitrobutyrolactone, which should be reducible to 2,2-dinitro-1,4-butanediol. Also under investigation are potentially short routes involving addition of mercuric nitroform to ethylene, ethylene oxide, or vinyl acetate. These reactions are summarized in the equations shown below.

$$C(NO_2)_3CH_2CH_2CN \xrightarrow{KOAc/50\%\ Dioxane} \begin{array}{l} \xcancel{} K^+\ {}^-C(NO_2)_2CH_2\underset{\underset{ONO}{|}}{C}HCN \\[2em] K^+\ {}^-C(NO_2)_2CH=CHCN \end{array}$$

$$C(NO_2)_3CH_2CH_2\overset{O}{\overset{\|}{C}}R \xrightarrow{KOMe} K^+{}^-C(NO_2)_2CH_2\underset{OH}{\overset{|}{C}H}\overset{O}{\overset{\|}{C}}R \dashrightarrow K^+{}^-C(NO_2)_2CH_2CHO$$

$$\downarrow NaBH_4$$

$$K^+{}^-C(NO_2)_2CH_2CH_2OH$$

$$C(NO_2)_3H \longrightarrow C(NO_2)_3CH_3 \longrightarrow K^+{}^-C(NO_2)_2CH_2CN \longrightarrow$$

$$\xrightarrow{BH_3} HOCH_2CH_2C(NO_2)_2CH_2OH$$

$$[C(NO_2)_3]_2Hg$$

$$\xrightarrow{CH_2=CH_2} [C(NO_2)_3CH_2CH_2]_2Hg \xdashrightarrow{OXIDATION} C(NO_2)_3CH_2CH_2OH$$

$$\xdashrightarrow{CH_2\overset{O}{-}CH_2} [C(NO_2)_3CH_2CH_2O]_2Hg$$

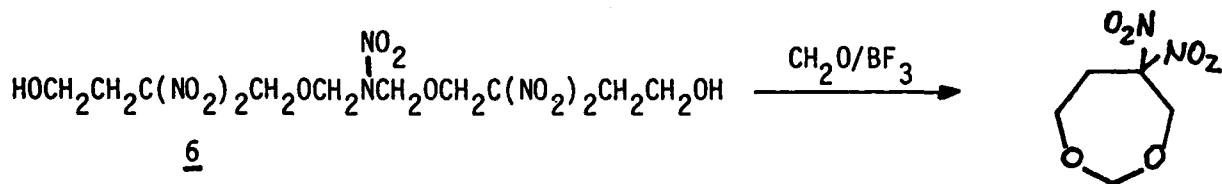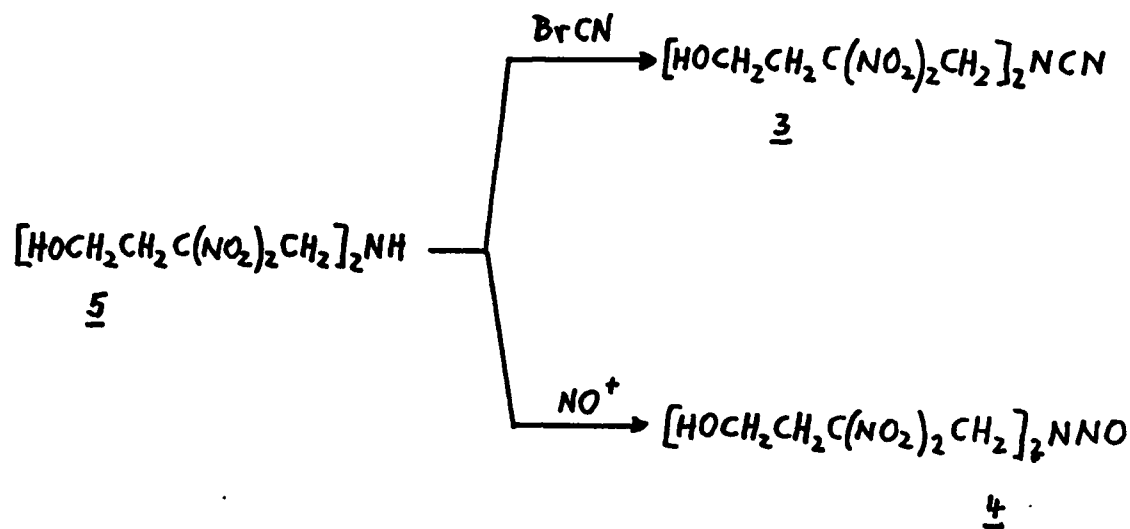$$\xdashrightarrow{CH_2=CHOAc} C(NO_2)_3CH_2CH\overset{OAc}{\underset{Hg-}{<}}$$
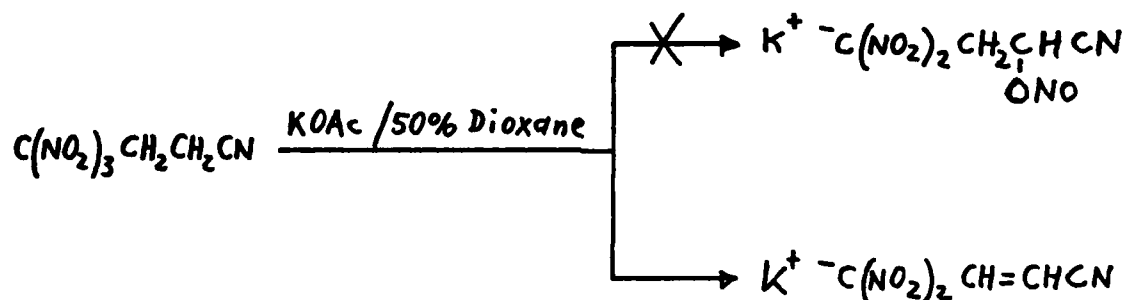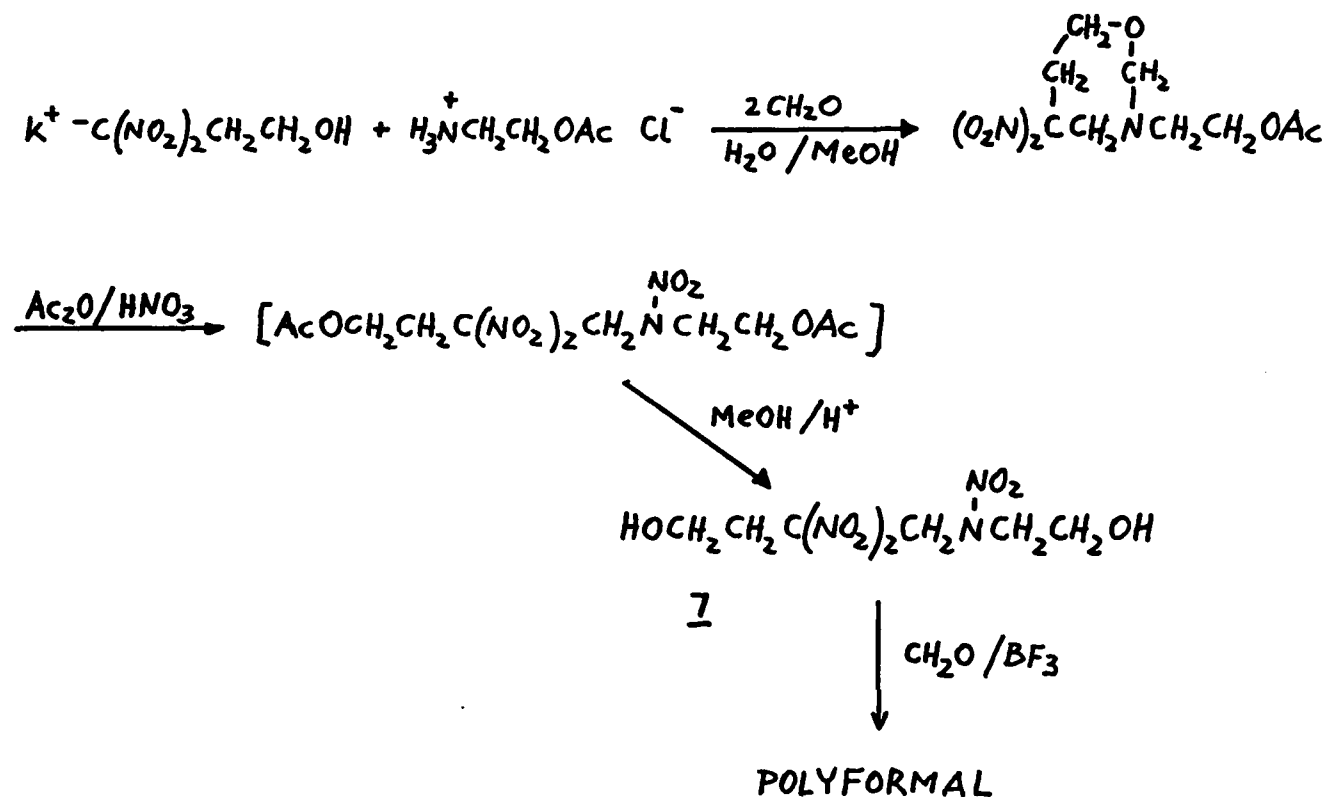
Another potentially simple route to 3,3-dinitropropanol has recently come
to our attention, but has not yet been tried. The individual steps are in the
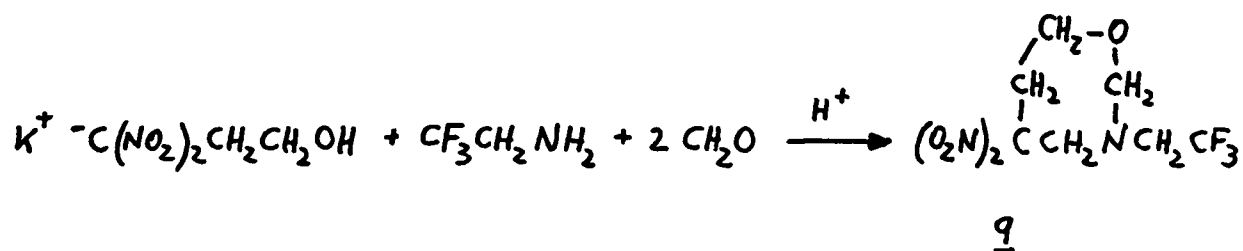Russian literature, in part without experimental details.

$$C(NO_2)_3H \xrightarrow{(Et)_3OBF_4} (O_2N)_2C=N(O)OEt \xrightarrow{CH_2=CH_2}$$

$$\xrightarrow[\text{aq. MeOH}]{KOH} K^+{}^-C(NO_2)_2CH_2CH_2OH$$

Several other diols derived from $\underline{2}$ which are of interest as building blocks for polyformals have been considered or synthesized. These include diols $\underline{3}$ and $\underline{4}$, which are closely related to $\underline{1}$ and can be prepared from the common intermediate $\underline{5}$. Diol $\underline{6}$ was synthesized under another task; on reaction with CH_2O/BF_3 etherate in sulfolane it underwent cleavage at an internal C-O bond to give a cyclic formal.

$$[HOCH_2CH_2C(NO_2)_2CH_2]_2NH \xrightarrow{BrCN} [HOCH_2CH_2C(NO_2)_2CH_2]_2NCN$$

$$\underline{5} \qquad\qquad \underline{3}$$

$$[HOCH_2CH_2C(NO_2)_2CH_2]_2NH \xrightarrow{NO^+} [HOCH_2CH_2C(NO_2)_2CH_2]_2NNO$$

$$\underline{4}$$

$$HOCH_2CH_2C(NO_2)_2CH_2OCH_2\overset{NO_2}{N}CH_2OCH_2C(NO_2)_2CH_2CH_2OH \xrightarrow{CH_2O/BF_3}$$
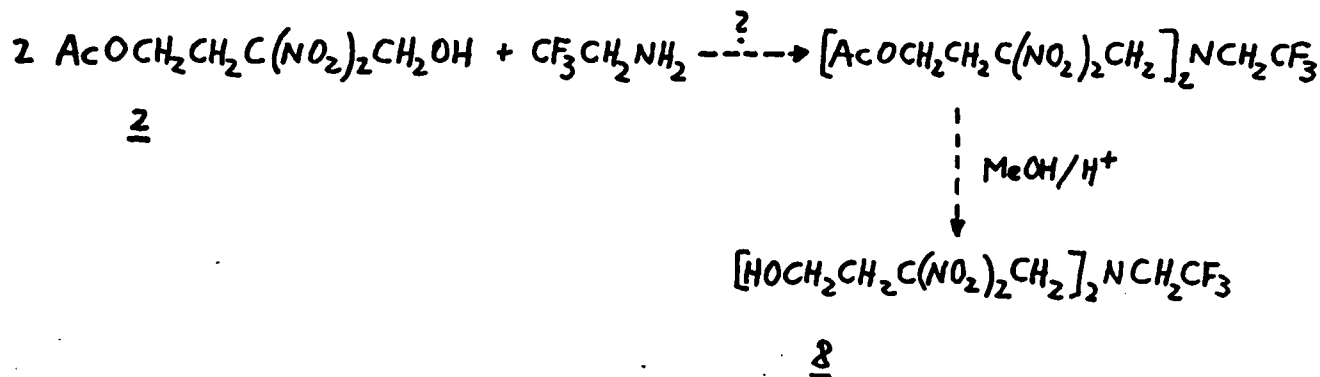
$$\underline{6}$$

9

Diol 7 was synthesized from potassium 3,3-dinitroethanol and aminoethanol acetate hydrochloride via Mannich condensation followed by nitrolysis and hydrolysis. Its reaction with CH_2O/BF_3 in sulfolane etherate gave a polyformal.

$$K^+ \; ^-C(NO_2)_2CH_2CH_2OH + H_3\overset{+}{N}CH_2CH_2OAc \; Cl^- \xrightarrow[H_2O/MeOH]{2\,CH_2O} (O_2N)_2\overset{\displaystyle CH_2-O}{\underset{\displaystyle \; }{C}}CH_2\overset{\displaystyle CH_2\quad CH_2}{\;}CH_2NCH_2CH_2OAc$$

$$\xrightarrow{Ac_2O/HNO_3} \left[AcOCH_2CH_2C(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2OAc \right]$$

$$\xrightarrow{MeOH/H^+}$$

$$HOCH_2CH_2C(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2OH$$

7

$$\downarrow CH_2O/BF_3$$

POLYFORMAL

Preliminary efforts have ben made to synthesize diol 8. The reaction of potassium 3,3-dinitropropanol with trifluoroethylamine gave only 9; however, the corresponding reaction with 2 appears more promising.

$$K^+ \; ^-C(NO_2)_2CH_2CH_2OH + CF_3CH_2NH_2 + 2\,CH_2O \xrightarrow{H^+} (O_2N)_2\overset{\displaystyle CH_2-O}{\underset{\displaystyle \;}{C}}CH_2NCH_2CF_3$$

9

10

$$2\ AcOCH_2CH_2C(NO_2)_2CH_2OH + CF_3CH_2NH_2 \xrightarrow{\ ?\ } [AcOCH_2CH_2C(NO_2)_2CH_2]_2NCH_2CF_3$$

$$\underline{2}$$

$$\downarrow MeOH/H^+$$

$$[HOCH_2CH_2C(NO_2)_2CH_2]_2NCH_2CF_3$$

$$\underline{8}$$

Also in the preliminary stage is an attempt to prepare polyformals from the fluorodiols $\underline{10}$ and $\underline{11}$. $\underline{10}$ is commercially available whereas $\underline{11}$ must be prepared from the corresponding dicarboxylic acid. So far, the reaction of $\underline{10}$ with CH_2O/H_2SO_4 has given a low yield (20%) of a polyformal which is liquid and readily soluble in FEFO.

$$HOCH_2(CF_2)_nCH_2OH \xrightarrow[H^+]{CH_2O} HOCH_2(CF_2)_nCH_2O-[CH_2OCH_2(CF_2)_nCH_2O]_m H$$
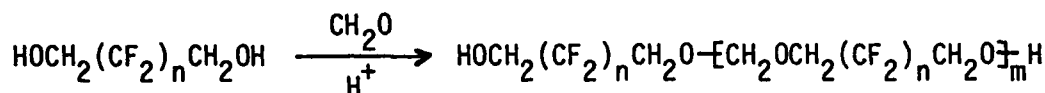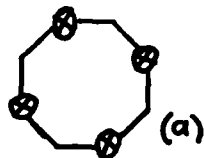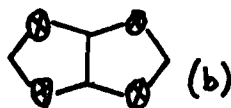
$\underline{10}$: n = 3
$\underline{11}$: n = 4

SYNTHESIS OF POTENTIALLY DENSE NITRAMINES

As outlined previously,[2] cyclic and polycyclic nitramines of the type (b) - (f) have calculated densities sufficiently higher than the calculated density of HMX to make such structures candidates for high energy-density explosives with predicted detonation pressures in the range of 420-470 Kbar. The first set of density values shown are for the all-nitramines, wheras the numbers in parentheses are for compounds in which half of the nitraza groups are replaced by gem-dinitro. Note the trend to higher densities with increasing number of rings in the molecule, and the increasing density difference between all-nitramine and mixed nitraza/gem dinitro compounds.
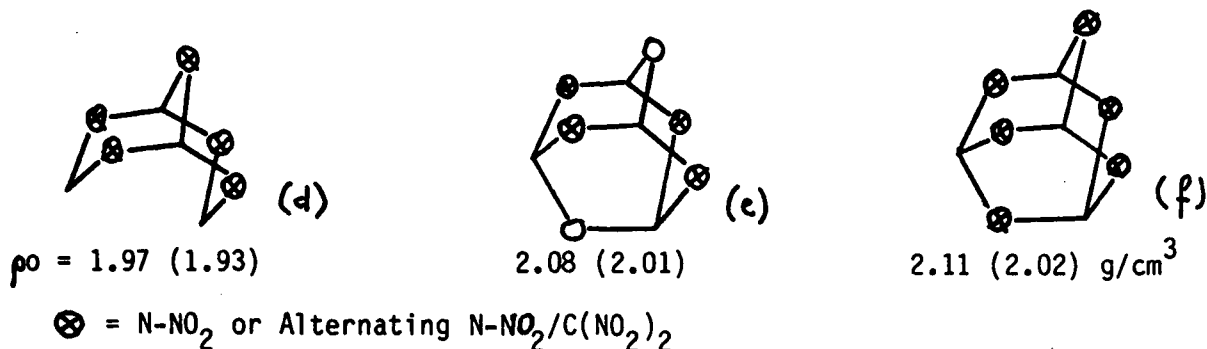
(a)   (b)   (c)

ρo = 1.79 (1.79)   1.91 (1.88)   2.05 (1.98) g/cm^3

ρo = 1.97 (1.93) (d)　　　2.08 (2.01) (e)　　　2.11 (2.02) g/cm^3 (f)
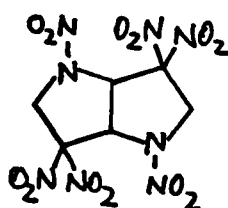
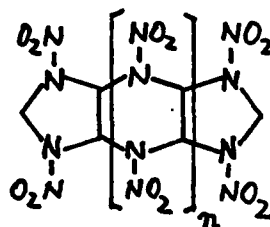⊗ = N-NO$_2$ or Alternating N-NO$_2$/C(NO$_2$)$_2$

During 1983 the previously initiated effort toward the synthesis of compounds of type (b), specifically bicylco-HMX, 12, the analog 13, and the linear polycyclic compounds 14 and 15, was continued. In addition, the synthesis and chemistry of potential precursors to structures (d) - (f) was studied.
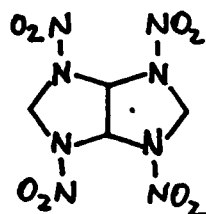

12　　　　　　　13　　　　　　　14: n=1　ρ_0 (calc'd) 1.95

　　　　　　　　　　　　　　　　　　15: n=2　"　　"　　1.96

The efforts toward the synthesis of bicyclo-HMX focused on the preparation and nitrolysis of 2,4,6,8-tetraacetyl-2,4,6,8-tetrazabicyclo-[3.3.0]octane, 16. While 16 could not be obtained by condensation of unprotected diacetyl dihydroxyimidazolidine with methylene-bis-acetamide (MBA), probably because of thermal fragmentation of the former, the diacetate and ditrifluoroacetate both condensed readily with MBA to give 16 in 72% and 30% yields, respectively.

MBA　　　　　　cis/trans ≃ 1:3　　　　　　16

12
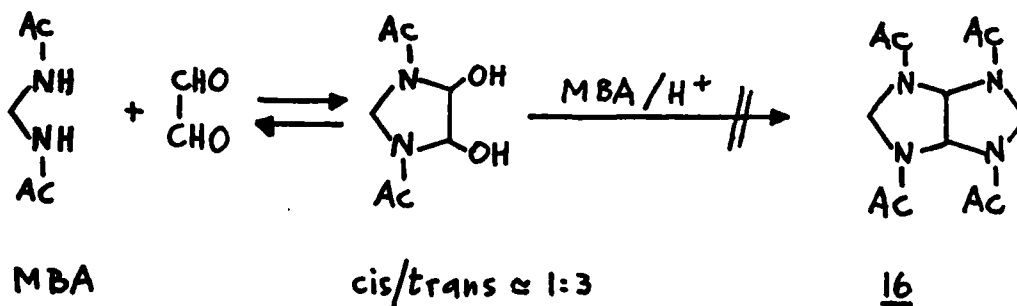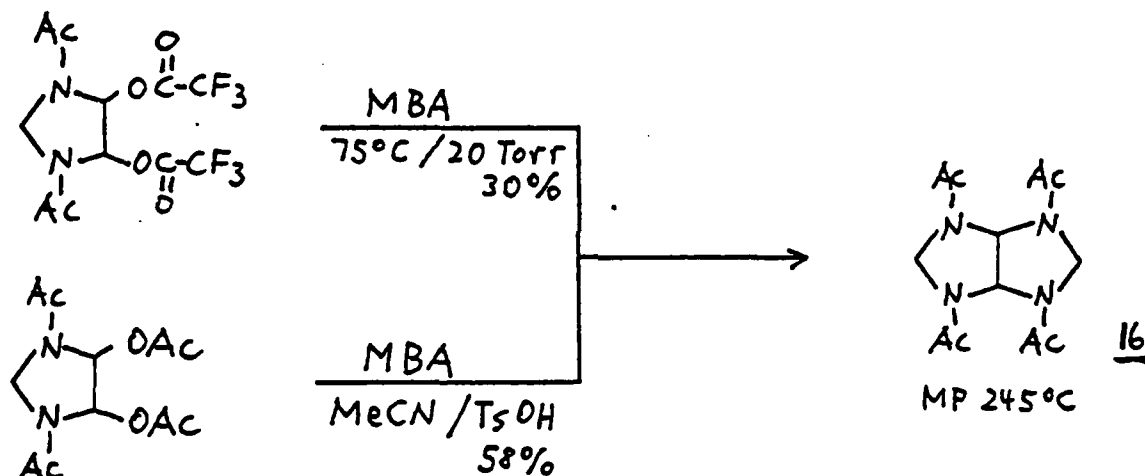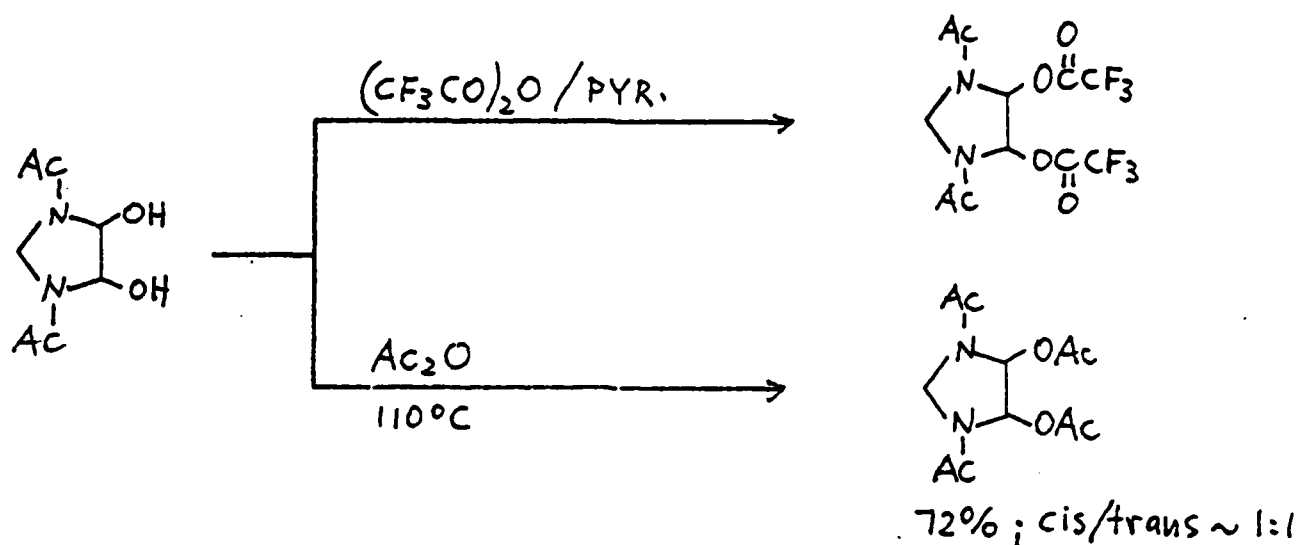
It was hoped that 16 would be amenable to nitrolysis to give bicyclo-HMX (12), and considerable effort was expended to achieve this transformation. The reagents and conditions tried are summarized below. In no case was a solid reaction product obtained although 16 had been consumed under most conditions. A possible explanation for this apparent failure of 16 to undergo acid nitrolysis in the desired fashion is ring-opening after initial quarternization of a ring nitrogen, a necessary first step in any nitrolysis process:


13
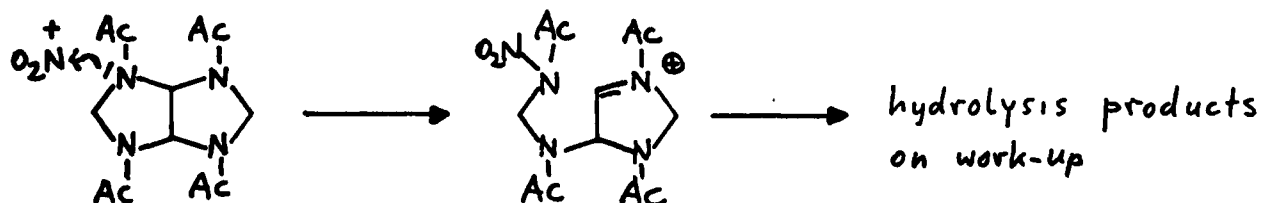
Attempted Nitrolysis of <u>16</u> to <u>12</u>:

<u>Reagent/Conditions</u>	<u>Result</u>
100% HNO_3/r.t./30 min.	Water-soluble oil + starting material
100% HNO_3/r.t./18 hr.	Water-soluble oil
100%HNO_3/Ac_2O/r.t./18 hr.	Water-soluble oil
100% HNO_3/conc. H_2SO_4/r.t./20 hr.	Water-soluble oil
100% HNO_3/CF_3SO_3H/CH_2Cl_2/0°/10 min.	Brown gum
100% HNO_3/CF_3SO_3H/CH_2Cl_2/r.t./30 min.	Brown gun
100% HNO_3/$(CF_3\overset{\overset{O}{\|}}{C})_2O$/r.t./3 hr.	Starting material and water-soluble oils
100% HNO_3/$(CF_3\overset{\overset{O}{\|}}{C})_2O$/r.t./16 hr.	Polymer + water-soluble oils
100% HNO_3/$(CF_3SO)_2O$/r.t./17 hr.	Water-soluble solid + oils
NO_2BF_4/MeCN/-30^oC/5 min.	Starting material + water-soluble oil
NO_2BF_4/MeCN/r.t./30 min.	Starting material + water-soluble oil
NO_2BF_4/MeCN/reflux/5 min.	Black tar

The ring-opening of <u>16</u> is undoubtedly aided by the presence of considerable ring strain. We currently believe that this may be an insurmountable obstacle and have abandoned reactions with <u>16</u> which would involve initial electrophilic attack on a nitrogen.

Other attempts to utilize <u>16</u> as an intermediate to <u>12</u> involved initial reaction at the carbonyl group of <u>16</u>. These reactions, which are listed in the following schemes, were also unsuccessful.

14

(a) Hydrolysis-Nitrosation:

$$\underline{16} \xrightarrow{\quad\quad X \quad\quad}$$
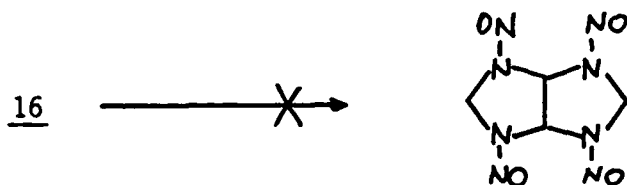
Reagent/Conditions	Result
$H_2O/K_2CO_3/(KSO_3)_2NO$	Some starting material recovered; water-soluble products
$H_2O/NaOH/(KSO_3)_2NO$ 3 days, r.t.	Some MBA and water-soluble products
$H_2O/Na_2O_2/NO$ 3 days, r.t.	MBA isolated
$H_2O/NaOH/NO$, Air 4 hr., r.t.	Water-soluble products

(b) Reduction:

$$\underline{16} \xrightarrow{\quad\quad X \quad\quad}$$
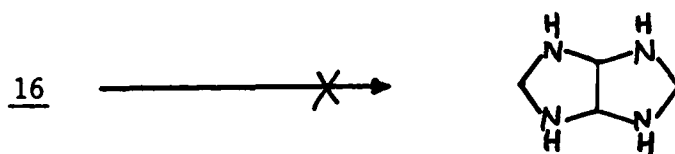
Reagent/Conditions	Result
$AlHg/H_2O$, r.t., 1 hr.	No reaction
Ca or Li/NH_3 (liq.) -33°C, 2 hr.	Some starting material + water-soluble amorphous polymer
$LiAlH(OEt)_3/THF$ reflux, 1 hr.	Water-soluble products and polymer; NMR complex
$LiAlH_4/ether/r.t.$, 4 hr.	Water-soluble products and polymer
$LiAlH_4/THF/reflux$, 1 hr.	polymer + small amount
$CH_3MgCl/THF/r.t.$, 4 hr.	Some starting material + water-soluble oil
n-BuLi/THF/r.t., 24 hr.	Starting material + oil + NH_3

15

(c) Hydrolysis/Ammonolysis:

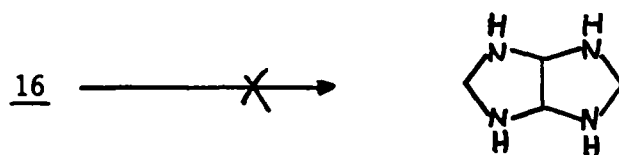$$\underline{16} \longrightarrow X \longrightarrow$$

Reagent/Conditions	Results
$NaOH/H_2O/r.t.$, 18 hr.	Water-soluble oil (NH_3)
$K_2CO_3/H_2O/reflux$, 2 hr.	Water-soluble oil (NMR complex)
$KOH/DMSO/H_2O/r.t.$	Water-soluble products (NH_3)
$NH_3aq./r.t.$, 18 hr.	No reaction
$NH_3/MeOH/r.t.$	No reaction
$NH_2NH_2/H_2O/reflux$, 17 hr.	red water-soluble oil (NMR complex)

The failure of these reactions may indicate that the tetrazabicyclooctane ring of $\underline{12}$ is not stable when one or more unsubstituted NH moieties are present, again probably due to the presence of ring strain.

A number of attempts were made to synthesize analogs of $\underline{16}$ which would be less susceptible to ring cleavage, or which would permit a different approach to introduction of nitro groups. These included condensation reactions of several methylene-bis-amides with glyoxal and 4,5-diacetoxy-1,3-diacetyl-imidazolidine, all of which were unsuccessful:

R = $SEt, OCH_2C_6H_5$

16
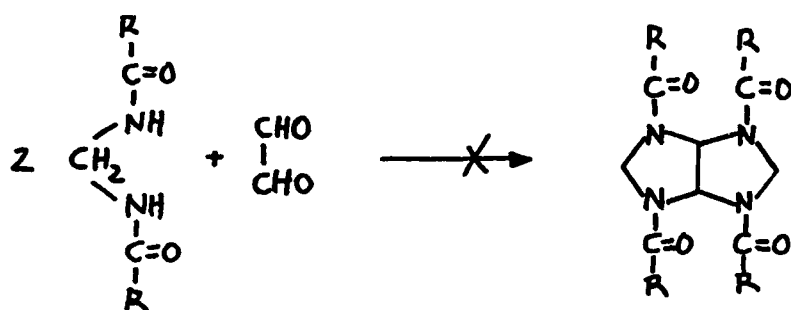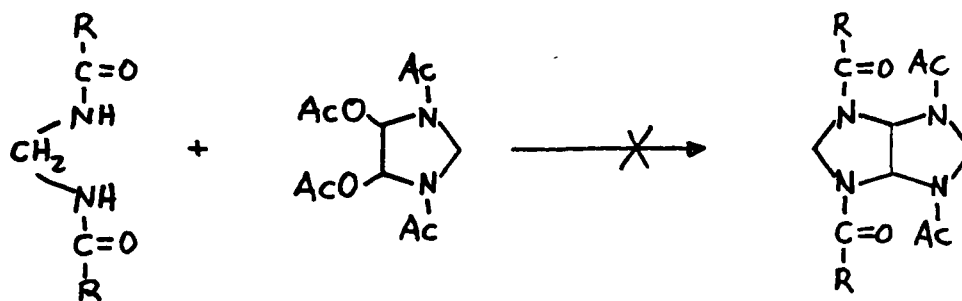
R = SEt, $OCH_2C_6H_5$

Details of reaction conditions are given in the experimental section.

A positive result from the above efforts is that a crystal density and structure of 16 has been obtained[5] which allows a more direct estimation of the density of bicyclo-HMX. The observed density of 16 is 1.37 and 1.38 g/cm^3 (2 polymorphs) vs. 1.34 g/cm^3 predicted by Holden's method.[6] Holden calculates a density of 1.91 g/cm^3 for bicyclo-HMX. Its actual density, therefore, may well be higher than that of HMX, and the compound remains a viable synthesis target.

In view of the difficulties encountered in the synthesis of the 2,4,6,8-tetrazabicyclooctane ring system and its chemical modification at the nitrogens, the effort was redirected toward the synthesis of the bicyclononane ring system 17 and compounds 14 and 15 derived from it. It was hoped that the 5 + 6 ring combination would be easier to assemble than the highly strained

17
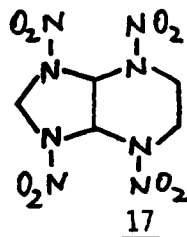
5 + 5 system in 16 and its analogs. As possible precursors to 14, 15, and 17, compounds of the type 18, 19, and 20 were sought,
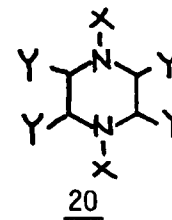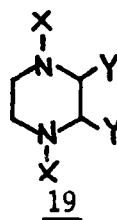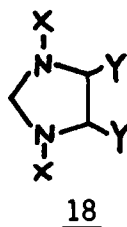
especially those with X = NO_2. 20 (X = CHO, Y = OAc, Cl, ONO_2) had been previously reported.[7] Attempts to convert 20c (X = CHO, Y = ONO_2) to the corresponding nitramine (X = NO_2) were not successful. Therefore,

17

condensation reactions of 20a (Y = OAc), 20b (Y = Cl), and 20c with methylene and ethylene-bis-amides were studied aimed at the synthesis of hexaazatricyclododecanes and tetradecanes 21.

$$\underline{20} \quad + \quad 2 \quad \longrightarrow \quad \underline{21}$$

n = 1,2
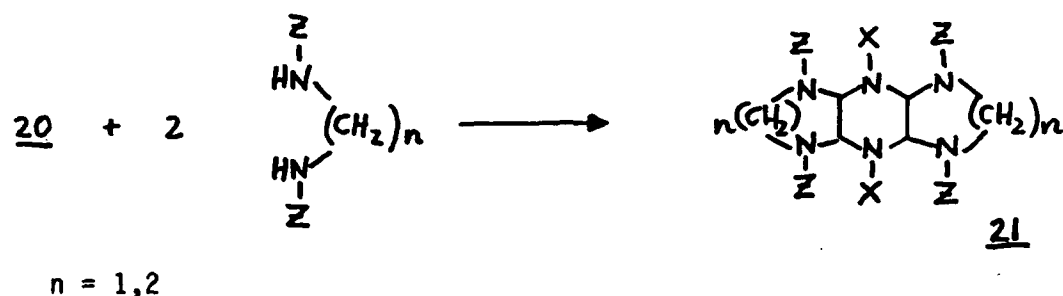
The following reactions were carried out:

$$\underline{20a} \quad + \quad 2 \quad \xrightarrow[\substack{\text{p-TsOH} \\ \text{reflux} \\ \text{3 days}}]{\text{MeCN}} \quad \text{only starting material isolated}$$

$$+ \quad 2 \quad \xrightarrow[\substack{\text{p-TsOH} \\ \text{reflux} \\ \text{18 hr.}}]{\text{MeCN}} \quad \text{only starting material isolated}$$

$$+ \quad 2 \quad \xrightarrow[\substack{\text{p-TsOH} \\ \text{reflux} \\ \text{18 hr.}}]{\text{MeCN}} \quad \text{only starting material isolated}$$

$$\xrightarrow[\substack{\text{ClCH}_2\text{CH}_2\text{Cl} \\ \text{reflux} \\ \text{18 hr.}}]{\text{BF}_3 \cdot \text{Et}_2\text{O}} \quad \text{dark oil; no solid}$$

18

$\underline{20b}$ + 2 [structure: H₂N-CH₂-CH₂-NH₂, drawn as CH₂ with NH₂ groups]
$\xrightarrow[\text{Et}_3\text{N}]{\text{MeCN}}$
r.t. 30 min.
reflux 5 min.
water-soluble oil

+ 2 [structure: O₂NHN-CH₂-CH₂-NHNO₂]
$\xrightarrow[\text{K}_2\text{CO}_3]{\text{MeCN}}$
r.t. 18 hr.
water-soluble oil
+ dark polymer

$\xrightarrow{\text{THF or DMSO}}$
r.t. 3 hr.
starting materials recovered

$\underline{20c}$ + 2 [structure: O₂NHN-CH₂-CH₂-NHNO₂]
$\xrightarrow[\text{p-TsOH}]{\text{MeCN}}$
reflux 24 hr.
water-soluble oil

$\xrightarrow[\text{KOH}]{\text{EtOH}}$
reflux 75 min.
water-soluble oil
+ starting material

No explanation can be given at present for the failure of these reactions.

Compounds $\underline{19}$ were obtained by the following sequence:

19
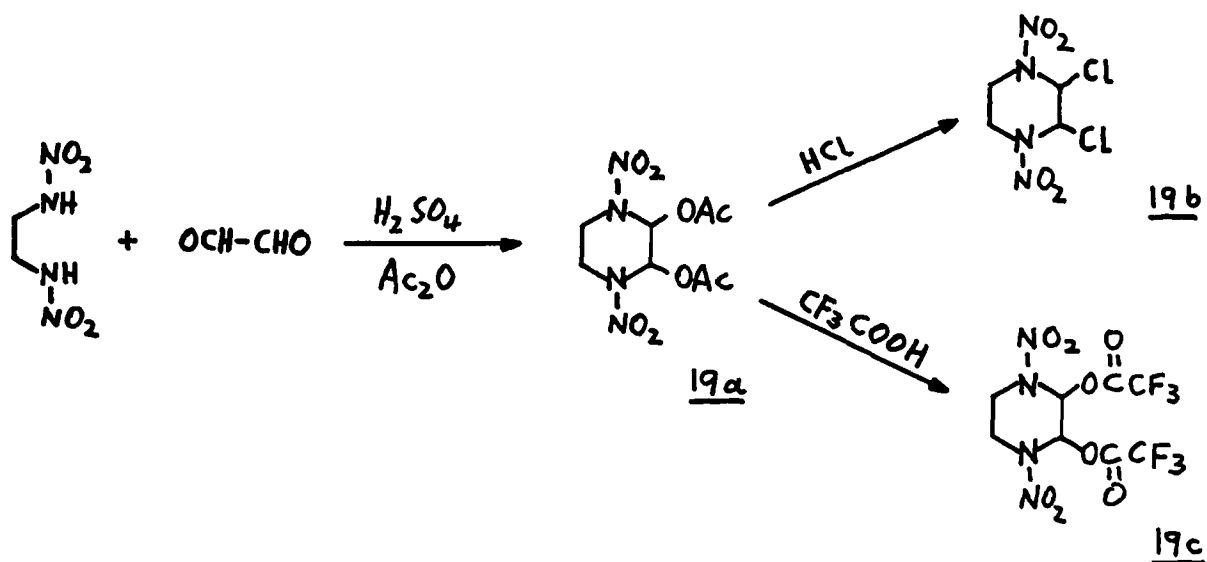
Condensation reactions of 19a-c leading to 17 are currently under investigation.

Towards the synthesis of compounds of the type (d) - (f), we have initiated a study of the reaction of the perhydrodiazocine 21 with bases and nucleophiles to determine if the tetrahydrodiazocines 22 can be generated. These species should be capable of undergoing transannular addition reactions leading to the bicyclononadiene ring system 23. Nitrolysis
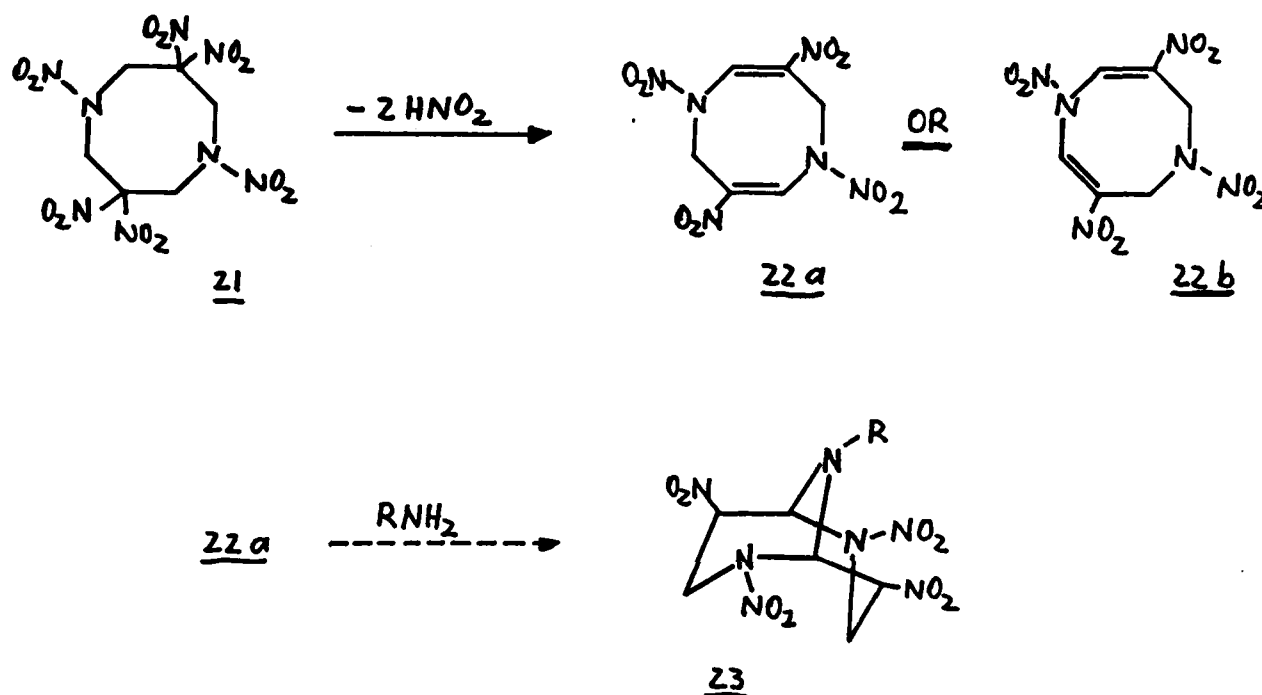
and nitration could lead to heptanitrotriazabicyclononane in several steps. 21 was found to be extremely reactive with all bases and nucleophiles tried except chloride ion. However, no pure reaction products have been isolated as yet.

Similar elimination reactions are being attempted with HMX, and N-halo derivatives of DPT and DAPT.
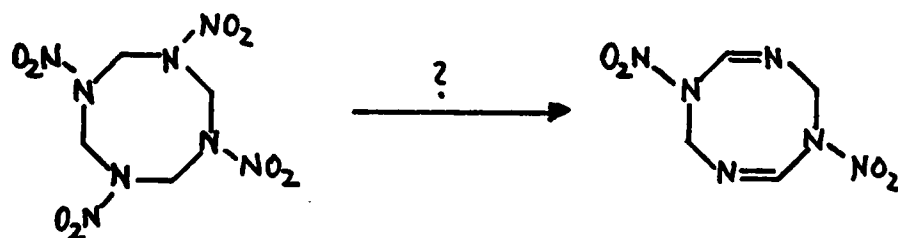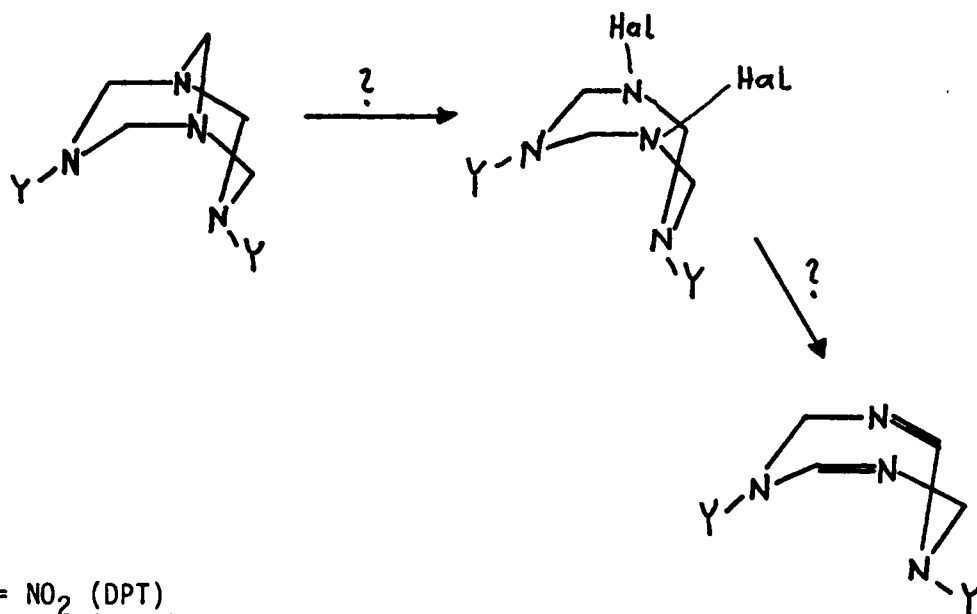
Y = NO$_2$ (DPT)
    Ac (DAPT)

We reported previously[1] on efforts to synthesize diaza- and oxaazadamantanes starting from cyclooctadiene. In this work the addition of N,N-dibromo-tert-butylamine to compounds 24 and 25 was studied further. It is believed that the desired addition reactions occur in low yield, but the products are mixtures of stereoisomers which have not yet been separated.

Ts = CH$_3$—⟨O⟩—SO$_2$

┿ = C(CH$_3$)$_3$

(2)

Hg(OAc)₂ / kI; I₂ $Hg(OAc)_2$, kI; I_2

3 ISOMERS → EXO, EXO → BASE → **25**

HCOOH

HO ... OH → MsO ... OMs

$+ NBr_2$

Br ... Br, N—+, O

≈ 10%

$Ms = CH_3SO_2$

$+ = C(CH_3)_3$
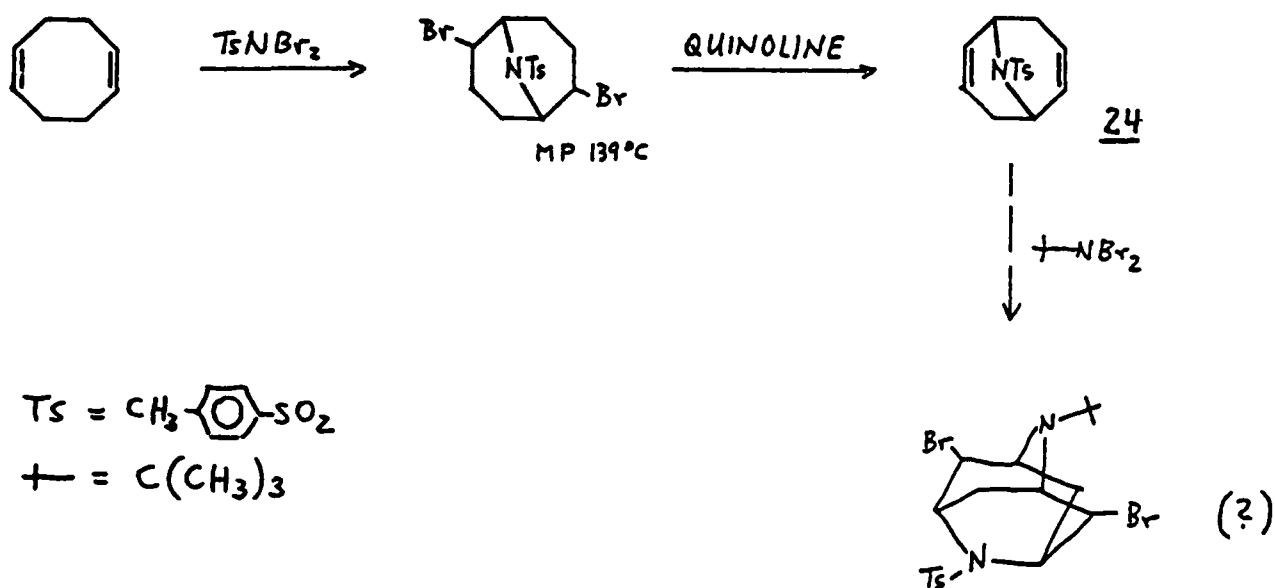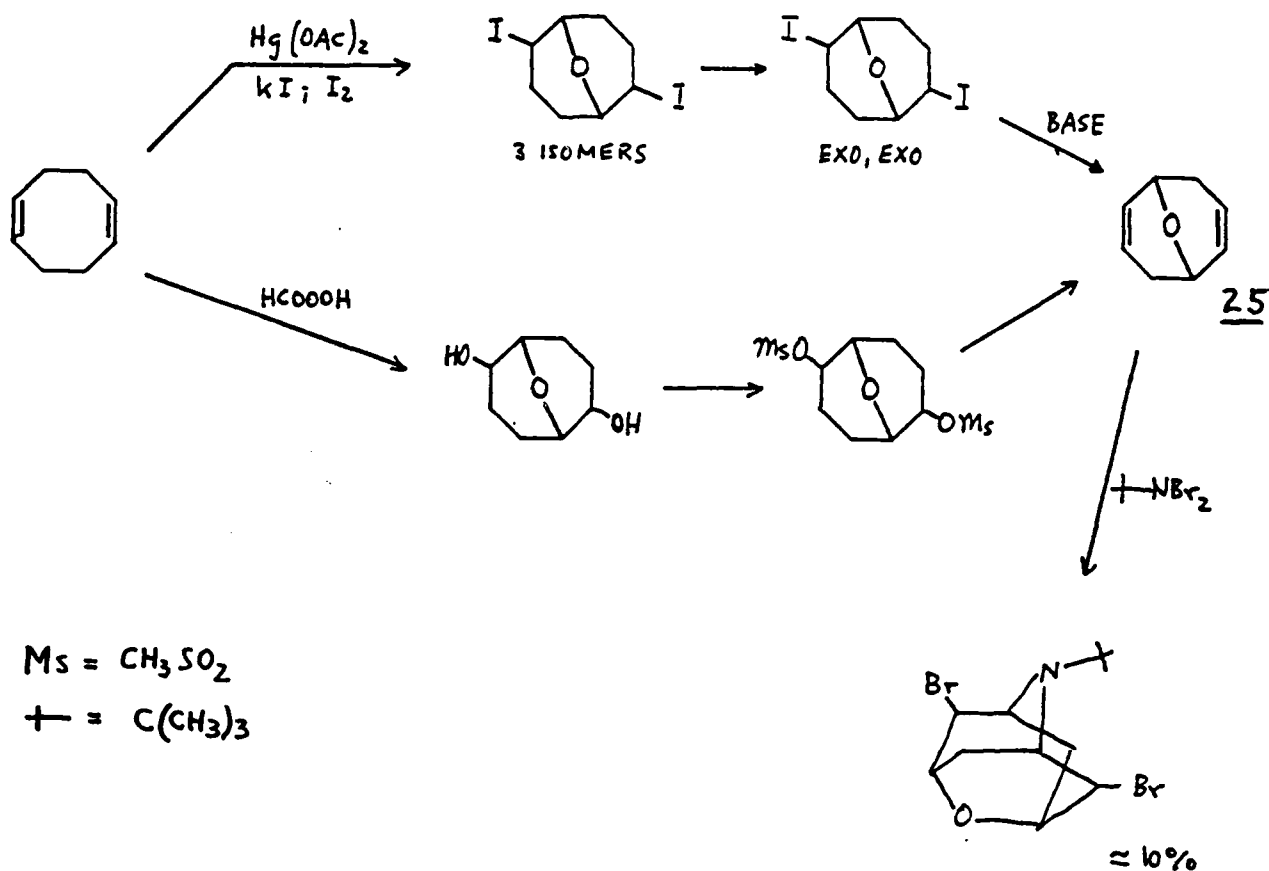
EXPERIMENTAL SECTION

Melting points are uncorrected; temperatures are in °C unless noted otherwise. Microanalyses are by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were obtained on a Varian EM-390 spectrometer; chemical shifts are in ppm relative to TMS as internal standard.

Polyformal of 1; Run 49/4. In a 15 ml three-neck flask, protected from moisture by a nitrogen atmosphere, 1 g diol 1 and 1 ml sulfolane were stirred until homogeneous. 69.9 mg trioxane was added and the mixture was again stirred until homogeneous. The solution was cooled in an ice bath, and 0.75 ml BF₃ etherate was added dropwise with stirring. Cooling was stopped and stirring continued for 20 hours. The mixture was diluted with 10 ml dichloromethane, poured into a solution of 0.9 g NaHCO₃ in 30 ml water, and this was agitated for 3 hours. The phases were separated; the organic layer was dried (MgSO₄) and stripped. The residue was mixed with 1.5 ml MeOH and added dropwise to a vigorously stirred mixture of 9 ml water and 4.5 ml MeOH. Stirring was continued until the liquid was clear; it was poured off and the precipitated polymer allowed to stand under 50 ml water overnight. The water was decanted and the polymer dissolved in 10 ml 1:1 dichloromethane/methyl acetate, the solution dried and stripped at 45°C for 4 hours. The residue was triturated overnight with a mixture of 13 ml dichloromethane and 8 ml hexane in a stoppered flask. After decanting the

22

solvent, the polymer was dried in vacuo. The weight of product ranged from 0.8 to 0.9 g.

Gel Permeation Chromotography, General Procedure. Analyses were performed using a Waters Model 6000A solvent delivery system and Model 440 ultraviolet (UV) absorbance detector operating at a wavelength of 254 nm. Two Varian Micropak TSK 3000H size exclusion columns were used: one 30 cm in length and the other 50 cm in length. The inside diameter of both columns was 0.75 cm. The packing pore size was 1500Å . The eluant was deaerated Burdick & Jackson tetrahydrofuran with water content less than 0.01% in order to maximize peak resolution. Solvent flow rate was nominally 0.5 ml/min also to maximize peak resolution. Chart speed was 1.0 cm/min. Data were collected by a Digital MINC microcomputer using a Chromatix CMX-10 dual channel interface module. Data reduction was performed with the Chromatix GPC2 software package. The sample (25-50 mg) was dissolved in 5 ml deaerated tetrahydrofuran, and 10 µl aliquot was injected with a M6K liquid chromatograph injector.

Determination of Hydroxyl Content for Polyformal of 1. Equivalent weights of polymer samples were determined using a Varian XL-200 fourier transform nuclear magnetic resonance (NMR) spectrometer according to the following procedure:

Known amounts of polymer (~50 mg) and trinitrobenzene (TNB) (~10 mg), which was used as an internal standard, were weighed into an NMR tube. Precision of weighing was to five decimal places to ensure adequate analytical reproducibility. 1 ml CD_3CN was added and the polymer was allowed to dissolve. Hexafluoroacetone was bubbled into the solution through a syringe needle for 2-4 minutes to achieve complete reaction of the polymer hydroxy groups. The terminal methylene groups were separated from the other methylene groups by this reaction and exhibited an isolated triplet at δ 4.07 ppm. This was integrated against the standard signal at δ 9.20 ppm.

Equivalent weights were then calculated according to the following equation:

$$\text{Eq. wt.} = 142 \times \frac{\text{wt. polymer}}{\text{wt. TNB}} \times \frac{I \text{ (TNB)}}{I \text{ (polymer)}}$$

where $I \equiv$ relative integration.

Curing Procedure for Polyformal of 1. To 4 g of a degassed solution of 1 part polymer and 2 parts FEFO was added 0.003 g dibutyl dilaurate; the mixture was stirred with a glass rod to solution, 0.1528 g PAPI 135 was added, and the mixture stirred again until homogeneous. The solution was degassed 30 minutes at 50°C and ≈1 Torr and then cured at 55°C. A well-cured gumstock was obtained after 36 hours. Some gas pockets were present in the gumstock.

3,3,7,7-Tetranitro-5-azanonane-1,9-diol diacetate. The procedure of ref. 2 was improved by more vigorous stirring and the use of a longer reaction time to allow all of the starting material to react. The product was obtained as a crystalline powder in 92% yield. Chilling of the crystallization mother liquor gave a semi-solid from which, by triturating with water, a second crop of product was obtained, bringing the total yield to 95%.

23

3-Nitropropyl Acetate. 167.0 g distilled 3-bromopropyl acetate was added to a well-stirred (mechanical stirrer) solution of 110.7 g sodium nitrite in 52 ml water and 640 ml DMSO. The mixture was stirred at $20 \pm 1^{\circ}$C. After 2 hours, a precipitate of NaBr formed, but the mixture remained stirrable. After ≃4 hours, sufficient ice-water was added to dissolve the precipitate (keep temperature below 25°C), and the solution was poured into water (total, 1750 ml). The product was extracted with 875, 700, and 525 ml dichloromethane, and the combined extract was washed four times with 875 ml water containing 100 g sodium chloride. After drying ($MgSO_4$), the solvent was removed to give 97 g of crude product which was used for further reaction without purification.

'H-NMR ($CDCl_3$) : δ 2.40 (t, 2 H), 4.27 (t, 2 H), 4.55 (t, 2 H) ppm.

2-(3-Bromopropoxy)tetrahydropyran. To 52.25 g 3-bromopropanol-1 was added 34.75 g dihydropyran at a rate to keep the temperature at 55°C. The mixture was then heated at 55°C for 2 hours. Volatiles were removed at 55°C/1 Torr for 2 hours to give the crude product which was ≃95% pure by GC.

2-(3-Nitropropoxy)tetrahydropyran. Following the above procedure for 3-nitropropyl acetate, 87.2 g crude 2-(3-bromopropoxy)tetrahydropyran was reacted with 46.9 g sodium nitrite in 14.66 ml water and 278.60 ml DMSO. After 7 hours, the mixture was poured into 975 ml water, the product was extracted with 3 x 250 ml dichloromethane, and the extract was washed with 4 x 250 ml water, dried ($MgSO_4$), and stripped to give 60.0 g crude product. This material was used in the oxidative nitration without further purification.

2-(3,3-Dinitropropoxy)tetrahydropyran. 3.15 g crude 2-(3-nitro-propoxy)tetrahydropyran was stirred with 9 ml 1 N sodium hydroxide with ice-cooling, and the solution was filtered with the aid of a small amount of Celite. With continued cooling, 0.79 g sodium nitrite was added, followed, after dissolution, by 5 ml ether and a solution of 3.9 g silver nitrate in 5 ml water. The mixture was stirred vigorously for 3 hours at room temperature; more ether was added and the mixture was filtered. The solid was washed with ether and the filtrate extracted twice with ether. The combined ether phases were dried ($MgSO_4$) and stripped to give 1.9 g crude product.

When the product was dissolved in 10 ml 1:1 methanol/ether and 3.25 ml 15% methanolic KOH was added with ice-cooling, 1.7 g potassium salt of the title compound was obtained after filtration and air-drying.

'H-NMR (D_2O) : δ 2.1 (broad s, 6 H), 3.65-4.6 (complex m, 7 H) ppm.

2 From Potassium 2-(3,3-dinitropropoxy)tetrahydropyran via Potassium 3,3-dinitropropanol-1. Potassium 2-(3,3-dinitropropoxy)tetrahydropyran (0.40 g, 1.5 mmol) was heated overnight with a solution of 10 ml MeOH and 2 ml of 3M HCl at 50°. Sodium sulfate, 2.0 g, was added and the solution filtered. This solution was treated with 5 M KOH/methanol (ice bath) until it tested basic with pH paper. The resultant yellow precipitate was collected and washed with ether to give 0.58 g crude potassium 3,3-dinitropropanol-1. The salt was heated in acetic acid (3 ml) up to 50° over a 20 minute period. Acetyl chloride (6 ml) was added and the solution was heated in a 55° bath overnight. The solution was poured into ice water, and after dichloromethane

extraction, removal of solvent, and dissolution of the crude acetate in methanol, the product was precipitated with KOH/methanol as above to give 0.25 g of yellow salt. This was dissolved in 8 ml H_2O and the pH adjusted to 3.2 with dilute HCl. Overnight stirring with 0.20 g formaldehyde solution (36%) gave, after CH_2Cl_2 extraction, 0.25 g (75%) of 2 which was pure by NMR analysis.

3-Nitropropyl nitrate from 3-nitropropyl acetate. 95 g of crude 3-nitropropyl acetate was dissolved in 300 ml methanol, 7 ml conc. HCl was added, and the mixture heated to 60-65°C for 24 hours. Stripping gave 62.5 g crude 3-nitropropanol. This was added with ice-cooling at <10°C to 187.5 ml 90% nitric acid, and the mixture stirred 0.5 hour at the same temperature. 125 ml conc. sulfuric acid was added at <10°C with stirring, the mixture stirred 1 hour with continued cooling and then drowned on crushed ice. Extraction with dichloromethane and usual work-up gave 78.5 g crude 3-nitropropyl nitrate.

'H-NMR ($CDCl_3$) : δ 2.53 (t, 2 H), 4.66 (2 overlapping triplets, 4 H) ppm.

Potassium 3,3-dinitropropanol-1 from 3-nitropropyl nitrate. 8 g crude 3-nitropropyl nitrate as prepared above was added with ice-cooling and stirring to a solution of 8 g potassium hydroxide in 40 ml methanol. The mixture was stirred 1 hour at ice-bath and 1 hour at ambient temperature, was cooled again and filtered. The product was washed with cold methanol and air-dried to give 5.88 g salt which was pure by NMR.

'H-NMR (D_2O) : δ 3.83 (t, 2 H), 4.40 (t, 2 H) ppm.

3,3-Dinitropropyl Acetate from Potassium 3,3-Dinitropropanol. 1.5 ml conc. sulfuric acid was diluted to 10 ml with ice-water; 10 ml ether was added followed by 4.15 g potassium 3,3-dinitropropanol which was added with ice-cooling and vigorous stirring. After 0.5 hour stirring at ice-bath temperature, the phases were separated and the aqueous layer was extracted twice with ether. After drying ($MgSO_4$), the ether was removed and 5 ml each dichloromethane and acetyl chloride was added. The solution was refluxed several hours, poured on ice, and the product extracted with dichloromethane. Usual work-up gave 2.75 g of 3,3-dinitropropyl acetate.

'H-NMR ($CDCl_3$) : δ 2.10 (s, 3 H), 2.58 (double t, 2 H), 4.36 (t, 2 H), 6.40 (t, 1 H) ppm.

By an alternative procedure, potassium 3,3-dinitropropanol-1 (0.60 g, 3.2 mmol) was stirred with 4 g acetic acid at 20° for 1 hour. Acetyl chloride (8 g) was then added and the solution heated in a 50° bath for 5 hours. Following the drowning of the solution, dichloromethane extraction, and removal of solvent, the crude acetate was precipitated from methanol by addition of KOH/methanol to give 0.50 g (68%) of potassium 3,3-dinitropropyl-1-acetate.

3-Bromopropyl Nitrate. To mixed acid (5 ml conc. H_2SO_4 and 0.55 ml 90% HNO_3) was added with cooling 2.8 g 3-bromopropanol. The mixture was stirred with ice-cooling for 1 hour, drowned, and worked up as usual to give 1.7 g product as a yellow oil.

25

'H-NMR (CDCl$_3$) : δ 2.32 (t, 2 H), 3.53 (t, 2 H), 4.70 (t, 2 H) ppm.

Reaction of 3-Bromopropyl Nitrate with Sodium Nitrate in Aqueous DMSO.
To a solution of 6.62 g sodium nitrate in 2.07 ml water and 39.3 ml DMSO was added at 20°C 10.15 g 3-bromopropyl nitrate, and the mixture was stirred 7 hours at the same temperature. The reaction was poured into 140 ml water, the product extracted with 3 x 40 ml dichloromethane, and the extracts washed with 4 x 40 ml water. Usual work-up gave 6.44 g oil which by NMR analysis contained only a small amount of the desired 3-nitropropyl nitrate. The main component in the 'H-NMR (CDCl$_3$) exhibited two triplets of equal intensity at δ 3.56 and 4.98 ppm.

2-Aminoethyl Acetate Hydrochloride.
8.2 g 2-Aminoethanol hydrochloride and 25 ml acetyl chloride was refluxed 24 hours, allowed to cool, diluted with dichloromethane, and the product collected by filtration. After drying over P$_2$O$_5$ in vacuo, the NMR spectrum showed the product to be the desired acetate hydrochloride.

'H-NMR (D$_2$O) : δ 2.70 (s, 3 H), 3.89 (t, 2 H), 4.95 (t, 2 H) ppm.

3-(2-Acetoxyethyl)-5,5-dinitroperhydroazoxepine.
11.65 g Formalin (36%), 87 ml water, 11.85 g potassium 3,3-dinitropropanol, and 3.57 g aminoethyl acetate hydrochloride were mixed with ice-cooling, then stirred at room temperature for 1.5 hours. Extraction with dichloromethane and usual work-up gave 13.35 g (76%) oil which by NMR was fairly pure title compound.

'H-NMR (CDCl$_3$) : δ 2.10 (s, 3 H), 2.80 (t, 2 H), 3.01 (t, 2 H), 3.95-4.20 (2t, 1s, 6 H), 4.34 (s, 2 H) ppm.

3,5,5-Trinitro-3-azaheptanediol-1,7 (7).
17.9 g of crude acetoxyethyl-dinitroperhydroazoxepine prepared as described above was mixed with 10 ml glacial acetic acid and added with stirring at 5-10°C to a mixture of 210.6 ml acetic anhydride and 63.2 ml 90% nitric acid (prepared at 20-25°C). After stirring 5 hours at ≈5°C, the mixture was poured into 1l ice-water, stirred vigorously for 1 hour, and the product extracted into dichloromethane. The oil obtained on usual work-up was mixed with 89 ml 70% aqueous methanol and 25 drops conc. hydrochloric acid and stirred at 65-70° overnight. After cooling, about 2/3 of the solvent was removed in vacuo, 100 ml water was added, and the product was extracted with ether. Drying and stripping gave 13.35 g crude diol as a viscous oil. The NMR spectrum showed no major inpurities, but a number of minor ones. Pure diol was isolated by chromatography on Silica (200 ml, EM Reagents Kieselgel 60) with dichloromethane-ethyl acetate 9:1 to 1:1 as eluant. The conditions for the chromatography were not optimized. About 7 g of solid diol was obtained plus 3-4 g of noncrystalline material. The solid fractions were recrystallized from dichloromethane. MP 50-51.5°C.

'H-NMR (CD$_3$OD) : δ 2.87 (t, 2 H), 3.70-4.15 (3t, 6 H), 5.23 (s, 2 H) ppm.

The diol was converted to the dinitrate by reacting with 100% nitric acid. MP 64-6°C.

'H-NMR (CD$_2$Cl$_2$) : δ 3.10 (t, 2 H), 4.19 (t, 2 H), 4.82 (double t, 4 H), 5.07 (s, 2 H) ppm.

Anal. Calc'd. for $C_6H_{10}N_6O_{12}$: C, 20.12; H, 2.81; N, 23.46%. Found: C, 20.40; H, 2.67; N, 23.19%.

4,5-Diacetoxy-1,3-diacetylimidazolidine. A mixture of 1,3-diacetyl-4,5-dihydroxyimidazolidine[8] (18.8 g, 0.1 mol) and acetic anhydride (100 ml) was refluxed for 30 minutes. The solution was then evaporated to dryness under reduced pressure to leave a residue which was triturated with ether (100 ml) and filtered to yield 20.8 g (76.4%) of white crystals: MP 136-139°C (partial melting) and then at 147-149°C. The 'H-NMR spectrum ($CDCl_3$) showed a mixture of cis and trans isomers in approximately equal proportions; δ 2.09 (m, CH_3s), 4.90 and 5.20 (AB quartet, cis-CH_2), 5.04 (s, trans-CH_2), 6.33 (s, trans-CHs), 6.35 and 6.54 (s, cis-CHs) ppm; mass spectrum (CI, CH_4) m/z 213 (100), 273 (M+1, 0.3), 301 (M+C_2H_5, 6), 313 (M+C_3H_5, 4).

Anal. Calc'd. for $C_{11}H_{16}N_2O_6$: C, 48.52; H, 5.92; N, 10.29. Found: C, 48,58; H, 6.02; N, 10.34.

cis-2,4,6,8-Tetraacetyl-2,4,6,8-tetraazabicyclo-[3.3.0]octane (16). A solution of 4,5-diacetoxy-1,3-diacetylimidazolidine (13.61 g, 0.05 mol), N,N'-methylenebisacetamide[9] (6.77 g, 0.052 mol), p-toluenesulfonic acid monohydrate (0.5 g), and CH_3CN (300 ml) was refluxed for 18 hours, and the solvent was then evaporated under reduced pressure. The residue was dissolved in hot CH_3OH (70 ml), cooled overnight in a refrigerator, and the solid filtered to yield 8.2 g (58%) of white crystals: MP 243-245°C; 'H-NMR (CD_2Cl_2) δ 2.07 and 2.30 (unsym. singlets, 12 H, CH_3), 4.48 and 5.54 (AB quartet, 4 H, CH_2), 6.25 (s, 2 H, CH) ppm; mass spectrum (CI, CH_4) m/z 212 (100), 283 (M+1, 17), 311 (M+C_2H_5, 4), 323 (M+C_3H_5, 4).

Anal. Calc'd. for $C_{12}H_{18}N_4O_4$: C, 51.05; H, 6.43; N, 19.85. Found: C, 50.95; N, 6.54; N, 19.86.

16 Via 4,5-Ditrifluoroacetoxy-1,3-diacetylimidazolidine. A mixture of 0.95 g 4,5-dihydroxy-1,3-diacetylimidazolidine,[8] 5 ml dichloromethane, and 0.8 g pyridine was cooled in an ice-bath under a nitrogen atmosphere, and 1.75 ml trifluoroacetic anhydride was added dropwise. The mixture was stirred at room temperature overnight, and the volatiles were removed in vacuo. 0.66 g Methylene-bis-acetamide[9] was added, and the mixture was stirred slowly while the reaction flask was evacuated to ≈20 Torr. After heating to 75-80°C in vacuo overnight and allowing to cool, 10 ml methanol was added and the mixture was kept at -10 to -20°C. 0.42 g (30%) of solid was collected by filtration. It was identical by NMR and MP with the material obtained above via the diacetate.

N,N'-Methylenebis-(benzyl carbamate). A mixture of benzyl carbamate (15.1 g, 0.1 mol), paraformaldehyde (1.50 g, 0.05 mol), p-toluenesulfonic acid monohydrate (190 mg, 1.0 mmol), and toluene (200 ml) was refluxed 30 minutes using a Dean-Stark trap to collect the water formed. The solution was cooled to 0°C and filtered to yield 6.3 g of white crystals: MP 137-140°C. Another 1.0 g of crystals were obtained by concentrating the toluene to 25 ml (total yield 46.5%). Recrystallization from CH_3CN gave colorless flat needles: double MP 149-150°C and 156-157°C; 'H-NMR ($CDCl_3$) δ 4.59 (t, 2 H,CH_2N), 5.16 (s, 4 H, CH_2O), 5.92 (br m, 2 H, NH), 7.43 (s, 10 H, arom) ppm.

Anal. Calc'd. for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; N, 8.91.
Found: C, 64.92; H, 5.86; N, 8.87.

N,N-Methylenebis-(ethylthiolcarbamate).

A mixture of ethyl thiolcarbamate (10.5 g, 0.1 mol), paraformaldehyde (1.50 g, 0.05 mol), sulfuric acid (3 drops), and toluene (150 ml) was refluxed for 1 hour using a Dean-Stark trap to collect the water formed. The mixture was filtered while still hot, then cooled to $0^{\circ}C$ and filtered to give 3.95 g of white plates: MP 158-159$^{\circ}C$. Concentration of the filtrate to 25 ml and diluting with isopropyl ether (25 ml) gave a second crop of crystals (1.28 g): MP 154-156$^{\circ}C$ (total yield 47%). Recrystallization from CH_3CN gave colorless flat needles: MP 159-160$^{\circ}C$; 'H-NMR ($CDCl_3$) δ 1.30 (t, 6 H, CH_3), 2.93 (q, 4 H, CH_2), 4.67 (t, 2 H, CH_2N), 6.69 (br m, 2 H, NH) ppm.

Anal. Calc'd. for $C_7H_{14}N_2S_2O_2$: C, 37.81; H, 6.35; N, 12.60; S, 28.84.
Found: C, 37.87; H, 6.43; N, 12.63, S, 29.00.

Conditions for Attempted Reactions of N,N'-methylenebis-(benzylcarbamate).

(a) With glyoxal: aqueous acetonitrile, hydrochloric acid, 1 hour reflux ⟶ no reaction; water, pH9, 2 days room temperature ⟶ no reaction; (b) with 4,5-diacetoxy-1,3-diacetylimidazolidine: acetonitrile, p-toluenesulfonic acid, 18 hours reflux ⟶ starting material plus water-soluble oil.

Conditions for Attempted Reactions of N,N'-methylenebis-(ethylthiolcarbamate).

(a) With glyoxal: glyoxal trimer, toluene, p-toluenesulfonic acid, 4 hours reflux ⟶ no reaction; aqueous THF, pH 8.5, 20 hours room temperature ⟶ no reaction; aqueous methanol, hydrochloric acid, 18 hours room temperature, 30 minutes reflux ⟶ no reaction; (b) with 4,5-diacetoxy-1,3-diacetylimidazolidine: acetonitrile, p-toluenesulfonic acid, 18 hours reflux ⟶ starting material plus water-soluble oil.

1,4-Diformyl-2,3,5,6-tetrahydroxypiperazine.[7]

A solution of glyoxal (435 g of aqueous 40% solution, 3.0 mol) and formamide (135 g, 3.0 mol) was adjusted to pH 8.6 with 10 N NaOH. The solution was stirred at room temperature for 18 hours, and the precipitated white solid was then filtered (16.5 g). The filtrate was adjusted to pH 8.6, stirred for 2 hours, and the precipitated solid was again filtered (150 g). The combined solids were triturated with hot 50% DMF-H_2O (200 ml) and filtered to yield 156 g (50.5%) of white solid which has no melting point, but which darkens at ~175$^{\circ}C$ and blackens above 195$^{\circ}C$; 'H-NMR (Me_2SO-d_6) δ 5.04 (s, 2 H, CH), 5.53 (s, 2 H, CH), 6.05 (br s, 4 H, OH), 8.32 (s, 2 H, CHO) ppm.

Anal. Calc'd. for $C_6H_{10}N_2O_6$: C, 34.95; H, 4.89; N, 13.59.
Found: C, 34.93; H, 4.88; N, 13.48.

1,4-Diformyl-2,3,5,6-tetraacetoxypiperazine.[10]

A mixture of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (10.3 g, 0.05 mol), acetic anhydride (100 ml), and sulfuric acid (0.3 ml) was heated at 100$^{\circ}C$ for 1 hour, then cooled and the solid filtered and washed with ether to yield 15.7 g (83.9%) of white crystals: MP 251-254$^{\circ}C$ dec. The analytical sample was recrystallized twice from CH_3CN: MP 259-260$^{\circ}C$ dec; 'H-NMR ($CDCl_3$) δ 2.12 (s, 12 H, CH_3), 6.13 (s, 2 H, CH), 6.89 (s, 2 H, CH), 8.57 (s, 2 H, CHO) ppm.

Anal. Calc'd. for $C_{14}H_{18}N_2O_{10}$: C, 44.92; H, 4.85; N, 7.49.
Found: C, 44.99; N, 4.83; N, 7.48.

1,4-Diformyl-2,3,5,6-tetranitratopiperazine.[10] To trifluoroacetic anhydride (6 ml) at 0°C was added 100% nitric acid (3 ml), followed by 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (1.03 g, 5 mmol). The mixture was stirred at 0°C for 15 minutes and then at room temperature for 1 hour. Methylene dichloride (25 ml) was then added and the precipitate filtered to yield 1.75 g (90.7%) of white solid; MP 144-145°C dec. Recrystallization from ethyl acetate-isopropyl ether gave white crystals: MP 151°C dec; 'H-NMR (Me_2CO-d_6) δ 7.27 (br s, 2 H, CH), 7.42 (br s, 2 H, CH), 8.87 (s, 2 H, CHO) ppm.

Anal. Calc'd. for $C_6H_6N_6O_4$: C, 18.66; H, 1.57; N, 21.77.
Found: C, 18.75; H, 1.58; N, 20.45.

1,4-Diformyl-2,3,5,6-tetrachloropiperazine.[10] A mixture of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (20.6 g, 0.1 mol), pyridine (1.58 g, 0.02 mol), and thionylchloride (200 ml) was refluxed for 75 minutes, then cooled and diluted with isopropyl ether (200 ml). The precipitate was filtered to yield 21.5 g (76.8%) of white crystals: MP 174-176°C dec. Recrystallization from ethyl acetate-hexane raised the MP to 189-190°C dec; 'H-NMR (Me_2CO-d_6) δ 6.83 (br s, 2 H, CH), 6.97 (br s, 2 H, CH), 8.93 (s, 2 H, CHO) ppm.

cis-2,3-Diacetoxy-1,4-dinitropiperazine (19a). A mixture of ethylene dinitramine (15.0 g, 0.1 mol), glyoxal (21.76 g of 40% aqueous solution, 0.15 mol), sulfuric acid (2.0 ml), and acetic acid (10 ml) was heated at 90-100°C for 20 minutes and then stirred for 30 minutes longer while the solution cooled to room temperature. The solution was then placed in a cold water bath while acetic anhydride (200 ml) was added dropwise over 20 minutes. After stirring at room temperature for 2 days, the mixture was filtered to give 9.70 g of white crystals: MP 206-208°C. An additional 4.25 g of product (MP 184-190°C) was obtained by evaporation of the filtrate to 50 ml under reduced pressure, adding isopropyl ether (25 ml), and cooling overnight in a refrigerator at 0°C. The total yield was 47.7%. The analytical sample, recrystallized from ethyl acetate-isopropyl ether, had MP 207-209°C; 'H-NMR (CD_2Cl_2) δ 2.05 (s, 6 H, CH_3), 3.76 and 4.52 (AB quartet, 4 H, CH_2, J = $8H_z$), 7.09 (s, 2 H, CH) ppm; mass spectrum (CI, CH_4) m/z 61 (100), 223 (M+1 - CH_3CO_2H, 59).

Anal. Calc'd. for $C_8H_{12}N_4O_8$: C, 32.88; H, 4.14; N, 19.17.
Found: C, 32.83; H, 4.14; N, 19.27.

cis-2,3-Dichloro-1,4-dinitropiperazine (19b). Dry HCl gas was bubbled into a mixture of cis - 2,3-diacetoxy-1,4-dinitropiperazine (2.92 g, 10 mmol) and ethyleneglycol (100 ml), cooled in a cold water bath, until saturated (~25 minutes). After stirring at room temperature for 3 days the solution was evaporated to dryness under reduced pressure and the residue triturated with isopropyl ether-hexane (1:1, 20 ml) and filtered to give 1.90 g of white crystals: MP 145-149°C. An additional 0.21 g of product was obtained by cooling the filtrate overnight in a refrigerator at 0°C. The total yield was

86%. The analytical sample was recrystallized from benzene-hexane: MP 148-150°C; 'H-NMR (CD_2Cl_2) δ 3.71 and 4.60 (AB quartet, 4 H, CH_2, J = 10 Hz), 6.83 (s, 2 H, CH) ppm; mass spectrum (CI, CH_4) m/z 209 (100), 211 (38), 245 [M+1 (Cl^{35}), 18], 247 (12), 249 (2), 273 (8), 285 (0.4).

Anal. Calc'd. for $C_4H_6Cl_2N_4O_4$: C, 19.61; H, 2.47; Cl, 28.94; N, 22.87. Found: C, 19.57; H, 2.48; Cl, 29.11; N, 23.06.

cis-1,4-Dinitro-2,3-bis(trifluoroacetoxy)piperazine (19c). A solution of cis-2,3-diacetoxy-1,4-dinitropiperazine (1.46 g, 5 mmol), trifluoroacetic acid (20 ml), and trifluoroacetic anhydride (5 ml) in CH_2Cl_2 (20 ml) was refluxed for 18 hours, then evaporated to dryness under reduced pressure, and the residue triturated with isopropyl ether (10 ml) and filtered to yield 1.81 g (90.5%) of white crystals: MP 141-143°C. The analytical sample was obtained by washing a sample of this product, in CH_2Cl_2, with aqueous 5% $NaHCO_3$ and recrystallizing this product from benzene-hexane: MP 144-145°C; 'H-NMR (CD_2Cl_2) δ 3.84 and 4.67 (AB quartet, 4 H, CH_2, J = 8 Hz), 7.38 (s, 2 H, CH); mass spectrum (CI, CH_4) m/z 128 (100), 287 (M+1 - CF_3CO_2H, 58), 429 (M+C_2H_5, 2).

Anal. Calc'd. for $C_8H_6N_4O_8$: C, 24.01; H, 1.51; F, 28.49; N, 14.00. Found: C, 24.18; H, 1.48; F, 28.34; N, 14.06.

REFERENCES

1. H. G. Adolph, W. M. Koppes, D. A. Cichra, and M. Chaykovsky, "Synthesis of Energetic Materials," Annual Progress Report for the Office of Naval Research, Mar 1983, Naval Surface Weapons Center, Silver Spring, MD 20910.

2. H. G. Adolph, W. M. Koppes, D. A. Cichra, and M. E. Sitzmann, NSWC MP-82-214 "Synthesis of Energetic Materials," Mar 1982.

3. L. A. Kaplan, J. Org. Chem. 29, 2256 (1964).

4. A. D. Nikoleava, L. K. Popov, and G. Kh. Kamai, Russian J. Org. Chem. 2, 1362 (1966).

5. R. Gilardi, Naval Research Laboratory, private communication.

6. D. Cichra, J. R. Holden, and C. Dickinson, NSWC TR 79-273, 19 Feb 1980.

7. ICI Industries Ltd. Annual Progress Report #18 for Contract N62558-4076 "Research on Ultrahigh Impulse Propellant Systems," Jan-Dec 1964.

8. S. L. Vail, C. M. Moran, H. B. Moore, and R. M. H. Kullman, J. Org. Chem. 27, 2071 (1962).

9. E. E. Gilbert, Synthesis 1,30 (1972).

10. Revised procedure from that given in ref. 7.

DISTRIBUTION

	Copies		Copies

Dr. L. V. Schmidt   1
Assistant Secretary of the Navy
(R, E, and S) Room 5E 731
Pentagon
Washington, DC 20350

Dr. A. L. Slafkosky   1
Scientific Advisor
Code RD-1
Commandant of the Marine Corps
Washington, DC 20380

Dr. Richard S. Miller   10
Code 432
Office of Naval Research
Arlington, VA 22217

Dr. David Siegel   1
Code 260
Office of Naval Research
Arlington, VA 22217

Dr. R. J. Marcus   1
Office of Naval Research
Western Office
1030 East Green Street
Pasadena, CA 91106

Dr. Larry Peebles   1
Office of Naval Research
East Central Regional Office
666 Summer Street, Bldg. 114-D
Boston, MA 02210

Dr. Phillip A. Miller   1
Office of Naval Research
San Francisco Area Office
One Hallidie Plaza, Suite 601
San Francisco, CA 94102

Mr. Otto K. Heiney   1
AFATL-DLDL
Eglin Air Force Base, FL 32542

Mr. R. Geisler   1
MKP/MS24
AFRPL
Edwards Air Force Base, CA 93523

Dr. F. Roberto   1
AFRPL MKPA
Edwards Air Force, CA 93523

Dr. L. H. Caveny   1
Air Force Office of
  Scientific Research
Directorate of Aerospace Sciences
Bolling Air Force Base
Washington, DC 20332

Mr. Donald L. Ball   1
Air Force Office of
  Scientific Research
Directorate of Chemical Sciences
Bolling Air Force Base
Washington, DC 20332

Dr. John S. Wilkes, Jr.   1
FJSRL/NC
USAF Academy, CO 80840

Dr. R. L. Lou   1
Aerojet Strategic Propulsion Co.
P.O. Box 15699C
Sacramento, CA 95813

Dr. V. J. Keenan   1
Anal-Syn Lab., Inc.
P.O. Box 547
Paoli, PA 19301

Dr. Philip Howe   1
DRDAR-BLT
Ballistic Research Laboratory
U. S. Army Armament Munitions
  and Chemical Command
Aberdeen Proving Ground, MD 21005

Mr. L. A. Watermeier   1
DRDAR-BLI
Ballistic Research Laboratory
U. S. Army Armament Munitions
  and Chemical Command
Aberdeen Proving Ground, MD 21005

Dr. W. W. Wharton   1
DRSMI-RKL
U. S. Army Missile Command
Redstone Arsenal, AL 35898

(1)

	Copies		Copies
Dr. A. Faulstich Code MAT-0716 Office of Naval Technology Washington, DC 20360	1	Mr. G. F. Mangum Thiokol Corporation Huntsville Division Huntsville, AL 35807	1
Dr. E. Zimet Code MAT-0712 Office of Naval Technology Washington, DC 20360	1	Mr. E. S. Sutton Thiokol Corporation Elkton Division P.O. Box 241 Elkton, MD 21921	1
Mr. Joe McCartney Naval Ocean Systems Center San Diego, CA 92152	1	Dr. G. Thompson Thiokol Corporation Wasatch Division	1
Dr. S. Yamamoto Marine Sciences Division Naval Ocean Systems Center San Diego, CA 91232	1	MS 240, P.O. Box 524 Brigham City, UT 84302	
Dr. G. Bosmajian Applied Chemistry Division Naval Ship Research and Development Center Annapolis, MD 21401	1	Dr. T. F. Davidson Technical Director Thiokol Corporation Government Systems Group P.O. Box 9258 Ogden, UT 84409	1
Dr. H. Shuey Rohm and Haas Company Huntsville Defense Contract Office Arthur Murray Building 723-A Arcadia Circle Huntsville, AL 35801	1	Dr. C. W. Vriesen Thiokol Elkton Division P.O. Box 241 Elkton, MD 21921	1
Dr. J. F. Kincaid KAMAN Sciences Suite 1200 1911 S. Jefferson Davis Highway Arlington, VA 22202	1	U. S. Army Research Office Chemical and Biological Sciences Division P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. J. Culver (SP-27311) Strategic Systems Project Office Propulsion Unit Washington, DC 20376	1	Dr. R. F. Walker DRDAR-LCE U. S. Army Armament Munitions and Chemical Command Dover, NJ 07801	1
Mr. E. L. Throckmorton (SP-2731) Strategic Systems Project Office Room 1048 Washington, DC 20376	1	Dr. R. G. Rhoades DRSMI-R U. S. Army Missile Command Redstone Arsenal, AL 35898	1
Dr. D. A. Flanigan Thiokol Corporation Huntsville Division Huntsville, AL 35807	1	Dr. W. D. Stephens Atlantic Research Corp. Pine Ridge Plant 7511 Wellington Road Gainesville, VA 22065	1

	Copies		Copies

Dr. A. W. Barrows 1
DRDAR-BLP
Ballistic Research Laboratory
U. S. Army Armament Munitions
  and Chemical Command
Aberdeen Proving Ground, MD 21005

Dr. C. M. Frey 1
Chemical Systems Division
P.O. Box 358
Sunnyvale, CA 94086

Professor F. Rodriguez 1
Cornell University
School of Chemical Engineering
Olin Hall, Ithaca, NY 14853

Defense Technical Information
  Center 12
DTIC-DDA-2
Cameron Station
Alexandria, VA 22314

Dr. Rocco C. Musso 1
Hercules Aerospace Division
Hercules Incorporated
Allegheny Ballistic Laboratory
P.O. Box 210
Washington, DC 21502

Dr. Ronald L. Simmons 1
Hercules, Inc.
AFATL/DLDL
Eglin Air Force Base, FL 32542

Dr. E. H. Debutts 1
Hercules, Inc.
Baccus Works
P.O. Box 98
Magna, UT 84044

Dr. James H. Thacher 1
Hercules, Inc.
Baccus Works
P.O. Box 98
Magna, UT 84044

Mr. Theodore M. Gilliland 1
Johns Hopkins University
Applied Physics Laboratory
Chemical Propulsion Information Agency
Johns Hopkins Road
Laurel, MD 20810

Dr. Jack Linsk 1
Code Org. 83-10, Bldg. 154
Lockheed Missiles and Space Co.
P.O. Box 504
Sunnyvale, CA 94088

Dr. B. G. Craig 1
NSP/DOD, MS-245
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545

Dr. R. L. Rabie 1
WX-2, MS-952
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545

Dr. R. Rogers 1
WX-2
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545

Mr. R. Brown 1
Code 330
Naval Air Systems Command
Washington, DC 20361

Dr. H. Rosenwasser 1
AIR-310C
Naval Air Systems Command
Washington, DC 20361

Mr. B. Sobers 1
Code 350
Naval Air Systems Command
Washington, DC 20361

Dr. L. R. Rothstein 1
Assistant Director
Naval Explosives Development
Engineering Department
Naval Weapons Station
Yorktown, VA 23691

Dr. Lionel Dickinson 1
Code D
Naval Explosive Ordnance
Disposal Technology Center
Indian Head, MD 20640

	Copies		Copies
Mr. C. L. Adams Code PM4 Naval Ordnance Station Indian Head, MD 20640	1	Mr. Lee N. Gilbert Code 3205 Naval Weapons Center China Lake, CA 93555	1
Mr. S. Mitchell Code 5253 Naval Ordnance Station Indian Head, MD 20640	1	Dr. E. Martin Code 3858 Naval Weapons Center China Lake, CA 93555	1
Dr. William Tolles Dean of Research Naval Postgraduate School Monterey, CA 93940	1	Mr. R. McCarten Code 3272 Naval Weapons Center China Lake, CA 93555	1
Code 6100 Naval Research Laboratory Washington, DC 20375	1	Dr. A. Nielsen Code 385 Naval Weapons Center China Lake, CA 93555	1
Dr. J. Schnur Code 6510 Naval Research Laboratory Washington, DC 20375	1	Dr. R. Reed, Jr. Code 388 Naval Weapons Center China Lake, CA 93555	1
Mr. R. Beauregard Code SEA-64E NC3, Room 11E08 Naval Sea Systems Command Washington, DC 20362	1	Dr. L. Smith Code 3205 Naval Weapons Center China Lake, CA 93555	1
Mr. G. Edwards Code SEA-62R32 CP6, Room 806 Naval Sea Systems Command Washington, DC 20362	1	Dr. B. Douda Code 5042 Naval Weapons Support Center Crane, IN 47522	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, PA 19112	1	Dr. R. Kelly Munitions Directorate Propellants and Explosives Defence Equipment Staff British Embassy 3100 Massachusetts Avenue Washington, DC 20008	1
Mr. C. M. Christensen Code SEA-62R2 CP6, Room 806 Naval Sea Systems Command Washington, DC 20362	1	Captain S. Shackelford AFRPL/LKLR Edwards Air Force Base, CA 93523	1
Dr. R. Derr Code 388 Naval Weapons Center China Lake, CA 93555	1	Dr. Merrill K. King Atlantic Research Corporation 5390 Cherokee Avenue Alexandria, VA 22314	1

	Copies		Copies
Dr. David C. Sayles Ballistic Missile Defense Advanced Technology Center P.O. Box 1500 Huntsville, AL 35807	1	Dr. R. A. Rhein Code 3244 Naval Weapons Center China Lake, CA 93555	1
Dr. Kurt Baum Fluorochem, Inc. 680 South Ayon Avenue Azusa, CA 91702	1	Dr. B. David Halpern Polysciences, Inc. Paul Valley Industrial Park Warrington, PA 18976	1
Professor J. H. Boyer University of Illinois Department of Chemistry Box 4348 Chicago, IL 60680	1	Dr. Karl O. Christe Rockwell International 6633 Canoga Avenue Canoga Park, CA 91304	1
Dr. Joyce J. Kaufman The Johns Hopkins University Department of Chemistry Baltimore, MD 21218	1	Dr. M. B. Frankel Rockwell International Rocketdyne Division 6633 Canoga Avenue Canoga Park, CA 91304	1
Dr. C. Coon University of California Lawrence Livermore National Laboratory P.O. Box 808 Livermore, CA 94550	1	Dr. D. L. Ross SRI International 333 Ravenswood Avenue Menlo Park, CA 94025	1
Professor Richard A. Reinhardt Naval Postgraduate School Physics and Chemistry Department Monterey, CA 93940	1	Mr. Ed van Ribbink Space Ordnance Systems 25977 San Canyon Road Canyon Country, CA 91351	1
Dr. J. Karle Code 6030 Naval Research Laboratory Washington, DC 20375	1	Mr. M. Baron (SP-27314) Strategic Systems Project Office Washington, DC 20376	1
Dr. R. Atkins Code 3852 Naval Weapons Center China Lake, CA 93555	1	Dr. G. M. Clark Department 4410 Aerojet Solid Propulsion Co. Sacramento, CA 95813	1
Dr. May L. Chan Code 3244 Naval Weapons Center China Lake, CA 93555	1		
Dr. T. B. Joyner Code 3264 Naval Weapons Center China Lake, CA 93555	1		